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1   **The Lindbladian Form**

2   **And**

3   **The Reincarnation of Felix Bloch's Generalized Theory of Relaxation**

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15   Abstract

16

17   The relationship between the classic magnetic resonance density matrix relaxation theories of Bloch and
18   Hubbard, and the modern Lindbladian master equation methods are explored.   These classic theories
19   are in full agreement with the latest results obtained by the modern methods. A careful scrutiny shows
20   that this also holds true for Redfield's later treatment, offered in 1965. The early contributions of Bloch
21   and Hubbard to rotating frame relaxation theory are also highlighted. Taken together, these seminal
22   efforts of Bloch and Hubbard can enjoy a new birth of contemporary relevance in magnetic resonance.

1. Introduction

In a recent and important publication, Bengs and Levitt (Bengs 2019) formalize NMR relaxation theory
for systems that deviate significantly from the equilibrium state, conditions that invalidate the high
temperature, weak ordering approximation, a corner stone in the commonly used Redfield theory
(Redfield 1957). Bengs and Levitt employed very modern methods that arose in the late 1970's and are
now fundamental in the topic of open quantum systems. These methods are often referred to
eponymously as the "Lindbladian Form". In addition to the work of Bengs and Levitt, a useful tutorial on
this topic can be found in the work of Manzano (Manzano 2020). Even though many, if not all of the
classic papers are cited in their offering of their own Lindbladian analysis, Bengs and Levitt were not
aware that a result identical to their own was already offered by Bloch (Bloch 1957), and masterly
expounded upon by Hubbard (Hubbard 1961). This conclusion can be ascertained by a glance at Table 1
of (Bengs 2019), where references to neither Bloch, nor Hubbard appear in the rightmost column. From
a study of past efforts, as reviewed by Bengs and Levitt along with their own results, this holds for
Abragam, for Jeener, and for Ernst. The significance of Bloch and Hubbard has gone unappreciated by
the NMR community for decades. By approaching the problem from a new perspective, and
importantly, with new experimental measurements on specially prepared spin systems, Bengs and Levitt
have resolved a long standing and long misunderstood issue.

This confusion over the results of Bloch and Hubbard is likely due, in part, to the use of difficult notation
by Bloch. Hubbard's treatment is a significant improvement but also possesses a few obscure aspects.
In that situation, it is not difficult to understand that nearly all NMR researchers rely on the simpler
Redfield formalism, especially given the fact that the conditions under which the approximations are
applicable, are those encountered in the vast majority of cases. Bengs and Levitt make a detailed
comparison between other proposals for a more proper relaxation theory that naturally contains the
correct equilibrium steady state, and all are found to be defective in one way or another. One argument
for the importance of Bengs and Levitt's effort, is their unequivocal and independent confirmation of
the success of Bloch and Hubbard over the other formulations. The claim, that a significant aspect of
relaxation theory, with an overcast coastline, now enjoys blue sky, is a fair one.

A *brief* exposition of Bloch's main results, by way of Hubbard, using Hubbard's own notation, appears
therefore to be a worthwhile endeavor, with historical importance and reasonable expectations that
such an effort will be of some interest to NMR researchers in general. How this task has fallen into the
hands of the author may also be of some help in orienting the reader.

The origins reside in the author's thesis work, a part of which involved the problem of anisotropic spin
lattice relaxation measurements for deuterated molecules dissolved in a liquid crystalline matrix. This
induced the author to study all the early papers on relaxation theory very carefully. Discovering the
significance of Bloch, and the clarity of Hubbard's exposition, left an indelible impression, even though
the author happily used the simpler Redfield formalism for the task at hand. The author abandoned the
field in 1988 to pursue other interests, but always enjoyed reading the current NMR relaxation
literature. Twenty five years later, a coworker gently persuaded the author to work out aspects of
relaxation and exchange during adiabatic sweeps (Barbara 2016). After completing that task, the author
reacquainted himself with Bloch and Hubbard in order to understand some lingering details. This effort
fully prepared the author to recognize how the work of Bloch and Hubbard tied into, and formed a
precedent for, the recent efforts of Bengs and Levitt.

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65   The main goal is then to *go beyond a citation*, and demonstrate the equivalence of the major result in
66   Bengs and Levitt to that of Bloch and Hubbard. The significant and original result offered here, is in the
67   mathematical analysis required to reveal the equivalent success of Bloch and Hubbard towards the
68   problem confronted and solved by Bengs and Levitt by their use of Lindbladian methods. The effort is
69   not trivial, and requires a careful study of Hubbard's notation and the development of symmetry
70   properties that Hubbard does not provide. Furthermore, Hubbard offers expressions that in some ways
71   are superior to the "fully reduced" Lindbladian form, as will be discussed in section 3. In the conclusion
72   section, the relation of these aspects of relaxation theory to later work by Redfield is commented on.

73   A discussion of the Lindbladian form is presented beforehand, from a simple and very direct approach
74   which possesses useful didactics, thereby allowing non experts to appreciate the essence of the
75   formalism without going into a full review of the mathematical details involved in a rigorous proof.
76   Since the Lindblad approach is rather new to the NMR literature, it can be helpful to have a more facile
77   presentation. Those readers interested in more details can find valuable sources in Bengs and Levitt,
78   Manzano and (Gyamfi 2020).

79   In addition to the Lindbladian form of Bloch's generalized theory of relaxation, we take advantage of the
80   opportunity to highlight Bloch's and Hubbard's early, and also largely unrecognized, contributions to the
81   dynamics of spin locking and rotating frame relaxation.   Together these aspects form a basis for a
82   renewed interest, or at the very least, a new and greater appreciation of these classic publications.

83

84   **2: A Guide to Lindblad**

85   The original publications on the Lindblad form are of a very mathematical flavor, both for the case of
86   finite dimensions, (Gorini 1976), as well as for a general Hilbert space (Lindblad 1976). Because of these
87   combined efforts, the Lindblad form is also often referred to as the GKSL equation. For finite
88   dimensional problems, as is pertinent to NMR applications, it is possible to offer a straightforward
89   method of construction, that is reasonably motivated and which uses elementary matrix algebra.   What
90   follows below is very much ex post facto, and was developed by the author after reading Bengs and
91   Levitt. It is not without precedent however. In an interesting historical overview of the Lindbladian
92   form (Chruscinski 2017), one can find examples of nearly identical approaches and even a very early use
93   of the Lindbladian form by Landau in 1927. For a very readable tutorial and overview, Manzano and
94   Gyamfi are recommended. For strictly mathematical proofs on the semi-group, Gorini and Lindblad
95   should be consulted. The reader should not interpret what follows as a replacement to the rigorous
96   mathematical if and only if proofs of the semi-group. The key to the approach is in the importance of
97   matrix factoring. Indeed, matrix factoring in terms of Kronecker products is an essential ingredient in
98   the mathematical proofs, but its role is not often explicitly highlighted in the manner given here. Matrix
99   products also arise in a straight forward manner when relaxation theory is approached by way of weak
100   coupling perturbation theory for the spin system and the bath, so that in this case the spin matrices are
101   already factored. Along the way, the simplest Lindbladian, the one used for exchange in NMR, and
102   which involves the factoring of the identity matrix, is presented.

103   As an *ansatz*, one can start from a *generalized* "state vector" dynamics, governed by a general complex
104   matrix M

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105
$$\dot{c}_\iota = \sum_j M_{ij}\, c_j \qquad (1)$$

106 In Eq.(1), M generalizes what is usually the Hamiltonian, so that the equation, in a purely analogous
107 manner, represents a type of "time dependent Schrodinger equation" for a finite number of states.
108 From the vector components c_i, we construct a Hermitian, rank-one "density matrix" with elements

109
$$\varrho_{ij} = c_i c_j^* \qquad (2)$$

110 The square of all rank-one matrices are proportional to themselves, $\varrho^2 = \alpha\varrho$, so that in this case $\alpha =$
111 $\Sigma c_i c_i^*$. However, keep in mind that the converse does not hold true. The terminology of "rank" has a
112 number of variants, and in this section we adopt the usage common in the theory of matrices (Halmos
113 1958).

114 The terms "state vector" and "density matrix" have been placed in quotation marks to emphasize their
115 heuristic labels at this early stage of the construction. The dynamics of this "density matrix" are given by

116
$$\dot{\varrho} = M\varrho + \varrho M^\dagger \qquad (3)$$

117 The solution to Eq.(3) can be expressed as

118
$$\varrho(t) = \Upsilon(t)\varrho(0)\Upsilon(t)^\dagger; \;\; \dot{\Upsilon}(t) = M\Upsilon(t); \;\; \Upsilon(0) = 1 \qquad (4)$$

119 Of course, $\Upsilon(t)$ is not unitary since M is not necessarily skew Hermitian. After some type of ensemble
120 averaging, the "density matrix" will *no longer be rank one* and will take on the character of a general
121 Hermitian matrix. This construction is a simple adaptation of the procedure delineated by Landau and
122 Lifschitz (Landau 1977). Conservation of probability $Tr(\dot{\varrho}) = 0$ does not hold for Eq.(3), but we are now
123 just two steps away from rectifying that shortcoming. An application of *Cartesian decomposition* allows
124 any matrix to be written in the form

125
$$M = -\tfrac{1}{2}H + A \qquad (5)$$

126 *H* is Hermitian, $H = H^\dagger$ and *A* is anti-Hermitian, $A = -A^\dagger$, which explains why the notation has been
127 used. The reason for the particular numerical factor of -1/2 in front of H will be revealed below. The
128 dynamics can then be expressed in terms of commutators [x,y] and anti-commutators {x,y}

129
$$\dot{\varrho} = -\tfrac{1}{2}\{H,\varrho\} + [A,\varrho] \qquad (6)$$

130 Only the anti-commutator term contributes to $Tr(\dot{\varrho}) = -Tr(H\varrho)$. If *H* possesses a non-trivial factoring
131 such that $H = NN^\dagger$, conservation of probability can be non-trivially restored by adding a term in $N^\dagger\varrho N$,
132 due to the cyclic properties of the trace operation $Tr(N^\dagger\varrho N) = Tr(NN^\dagger\varrho)$. The augmented dynamics
133 are then transformed into the famous Lindbladian form:

134
$$\dot{\varrho} = -\tfrac{1}{2}\{NN^\dagger,\varrho\} + [A,\varrho] + N^\dagger\varrho N \qquad (7)$$

135 The matrix factoring adopted above is known in the numerical matrix analysis literature as Cholesky
136 decomposition (Press 1992) and is closely related to polar decomposition, where an arbitrary linear
137 transformation can be written as a product of a positive matrix and an isometry (Halmos 1958). While
138 positive, it may not be completely positive. The condition of complete positivity requires that the

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139　　Kronecker product of the matrix with the identity matrix of arbitrary dimension also be positive [3]. This
140　　condition has been essential for a strict mathematical proof and also ensures that the density matrix has
141　　real, positive eigenvalues. Complete positivity has been critiqued in (Pechukas 1994) and (Shaji 2005).

142　　According to Eq.[4], the commutator part *and* the anti-commutator part of Eq.[7] can be eliminated
143　　from Eq.[7] by the usual method of performing an interaction contact transformation, which then
144　　produces a new dynamical equation $\dot{\varrho}' = kV^{\dagger}(t)\varrho'V(t)$. The choice of scaling in Eq.[6] is made so that
145　　k=1. Throughout the steps used to construct Eq.[7], no assumptions regarding the time dependence of
146　　the operators are made, and therefore a semi-group structure, where the total propagation must
147　　satisfy $T(t_2 + t_1) = T(t_2)T(t_1)$ does not constitute an essential requirement in this *construction* of the
148　　Lindbladian form. This provides some evidence that the exercise offered above is something more than
149　　merely an effort to cut corners.

150　　It is interesting to compare conservation of probability for the density matrix, $Tr\dot{\varrho} = 0$, with that for
151　　pure states, $\frac{d}{dt}\sum c_i c_i^* = 0$. This is a more strict condition and holds if and only if $M^{\dagger} = -M$ as is usual
152　　for unitary quantum state evolution with conservation of probability where $\sum c_i c_i^* = 1$ and M can be
153　　written as $i\mathcal{H}$ where $\mathcal{H}$ is now the Hamiltonian. By incorporating this condition into a higher
154　　dimensional structure, we enjoy greater latitude in having Hermiticity and probability conservation
155　　along with richer dynamics that can represent relaxation effects.

156　　The anti-Hermitian part of Eq.(5) has a trace preserving, Hamiltonian evolution and can be taken to
157　　represent relaxation induced, or so called, *dynamic frequency shifts*. These are often small in NMR
158　　applications, but not exclusively so. A review of these effects in NMR can be found in (Weberlow 1996),
159　　and this aspect will not be pursued further here.

160　　The Lindbladian form is often written as above, but it is important to recognize that it can be expressed
161　　in terms of commutators, as was used in the original work by Gorini et.al.

162
$$[N, \varrho N^{\dagger}] + [N\varrho, N^{\dagger}] = -\{N^{\dagger}N, \varrho\} + 2N\varrho N^{\dagger} \qquad (8)$$

163　　In this equation, the alternative factoring, $H = N^{\dagger}N$ has been adopted. If N is a normal
164　　matrix, $[N^{\dagger}, N] = 0$, the ordering is not important, and in this case, the identity matrix, which
165　　corresponds to an infinite temperature limit to within a scalar factor, is a steady state. A similar
166　　example is afforded by the factoring given by $H = \{H_1, H_2\} = H_1 H_2 + H_2 H_1$ where both matrices are
167　　Hermitian. The resulting expression can be written in terms of nested commutators:

168
$$\big[[H_1, \varrho], H_2\big] + \big[[H_2, \varrho], H_1\big] \qquad (9)$$

169　　The anti-commutator can also be re-expressed as a difference between $S^2 = (H_1 + H_2)^2$ and $D^2 = $
170　　$(H_1 - H_2)^2$ and the above equation can written as the combination

171
$$[S\varrho, S^{\dagger}] + [S, \varrho S^{\dagger}] - \big([D\varrho, D^{\dagger}] + [D, \varrho D^{\dagger}]\big) \qquad (10)$$

172　　Even though *S* and *D* are both Hermitian, Hermitian conjugates have been kept explicit in order to
173　　conform with Eq.[8]. One simple method for constructing a non-normal factoring is to insert the identity
174　　between factors. Write $H = P^2 = Pe^{iQ}e^{-iQ}P$ with $[P, Q] \neq 0$ so that $N = Pe^{iQ}$ and $N^{\dagger} = e^{-iQ}P$. Of
175　　course, Q must be Hermitian in order to preserve the Hermitian character of the density matrix in Eq.(7).
176　　Non-normal expansions are also generated quite naturally when spectral decomposition is employed.

177 That procedure will be treated in the next section when the operator expansions of Bloch and Hubbard
178 are discussed.

179 While a non-trivial factoring excludes the identity matrix as a sole factor, the identity matrix itself can
180 often be factored. If $H = 1 = RR$ the Lindbladian is now the traditional expression used for the
181 description of intramolecular exchange processes in NMR (Alexander 1962)

182
$$k(R\varrho R - \varrho) \qquad (11)$$

183 In equation 11, the constant k is now used to denote the rate of exchange. The case of *intermolecular*
184 exchange is considerably more complicated, and is generally nonlinear, unless high temperatures and
185 small deviations from equilibrium hold forth (Alexander 1962). It is worth pointing out here that in the
186 literature on the Lindbladian form the N operators used are often referred to as "jump operators"
187 (Manzano 2020).

188 The use of Cartesian decomposition in Eq.(5) is not actually necessary. If M can be factored, for
189 example, as the product, $AB^{\dagger}$, one can directly write down

190
$$\dot{\varrho} = AB^{\dagger}\varrho + \varrho BA^{\dagger} - A^{\dagger}\varrho B - B^{\dagger}\varrho A \qquad (12)$$

191 Or

192
$$\dot{\varrho} = -\{[B^{\dagger}\varrho, A] + [A^{\dagger}, \varrho B]\} \qquad (13)$$

193 This non-Hermitian, mixed form is useful when comparing Lindbladian expressions with the early
194 relaxation theories of Bloch and Hubbard. In these, the use of spherical tensor operators can obscure
195 the Hermitian character of certain expressions and also produce expressions that on first blush, do not
196 appear to be strictly Lindbladian.

197 Given that there are n^2-1 independent matrices excluding the identity matrix, we can expect to have a
198 linear combination of Linbladian forms, with coefficients that are not related in a rank one fashion, just
199 as with the density matrix. These coefficients represent generalized transport parameters.

200 Whereas this guide to Lindblad should be sufficient for practical purposes, the author is aware that
201 some readers will be left unsatisfied or perhaps adamantly critical. Therefore, while it was not the
202 author's original intention, some elaboration is offered in the appendix.

203 The constraints of the Lindbladian form, though powerful, do not provide a complete theory of
204 irreversibility. Other considerations must be brought to bear on the exact manner in which a
205 complicated, many body theory that is fundamentally reversible, can be reduced to a simpler, but now
206 apparently irreversible one. Assumptions of weak coupling between systems (spins and bath) and loss
207 of long time scale correlations as applied to perturbation theory, are common elements throughout
208 both modern Lindbladian and the Bloch Hubbard approaches. Additionally, the need to invoke the
209 secular approximation is paramount all such approaches, as will be discussed in the next section.

210 **3. Bloch-Hubbard Relaxation Theory and the Lindbladian Master Equation**

211 As announced in the introduction, is not the author's goal to give an in depth review of the Bloch-
212 Hubbard theory. In particular, Hubbard's exposition is especially clear on most accounts, and those with
213 sufficient interest can directly consult the original publications. Rather, the intention is to provide

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214   reasons and the motivation for others to read or revisit these classic works. It is useful to point out here
215   at the outset that many of the mathematical methods used with modern Lindbladian approaches to
216   Markovian systems are exactly those used by Bloch and Hubbard, and other aspects of this fact will be
217   emphasized in the conclusions. Since the success of the Bloch-Hubbard theory has gone unrecognized
218   for so many years, and has now been brought into the limelight by the work of Bengs and Levitt, a
219   demonstration of the equivalence can be considered an original contribution to the topic.

220   We can start with Equation [100] of Hubbard's excellent review article of Bloch's generalized theory:

221
$$R(\sigma) = \sum_{kls} \operatorname{sech}(\beta\omega_s^l/2) J_{lk}(\omega_s^l)\{[O(-\beta)V_s^l O(\beta)\,\sigma, V^k] - [\sigma\,O(\beta)V_s^l O(-\beta), V^k]\} \quad (14)$$

222   Here we now adopt the notation used by Hubbard and the reader should keep this change in mind.
223   Hubbard uses σ to denote the spin density matrix. The V_s^l operators act on the spin states, and a fuller
224   description of them will be given shortly, as well as how the frequencies ω_s^l are determined by the
225   eigenvalues of the spin Hamiltonian E. The operator, $O(\beta) = \exp(\frac{\beta E}{2})$ is related to the equilibrium value
226   of the density matrix. Clearly, $R(\sigma)$ is linear in σ, and as Hubbard points out, it is easy to see that if the
227   density matrix is at equilibrium, $R(\sigma_{eq}) = 0$. The commutator form of Hubbard's equation above is
228   very suggestive. It is almost Lindbladian, but not quite the same as the canonical form.

229   The sums in Eq.(14) are over integer steps from –n to +n for each index, with different values of n for
230   (k,l) and s. The indexed operators and frequencies satisfy symmetries for negative and positive values of
231   their indices:

232
$$(V_s^l)^\dagger = V_{-s}^{-l}; \quad \omega_{-s}^{-l} = -\omega_s^l; \quad V^l = \sum_s V_s^l \quad (15)$$

233   In order to manipulate Hubbard's expression, we also need some symmetry properties of the $J_{kl}(\omega)$.
234   These index symmetries follow in a straightforward manner from their definitions, which for
235   completeness, and also adhering to Hubbard's original notation, we list.

236
$$J_{lk}(\omega) = \frac{1}{2}\int_{-\infty}^{\infty} d\tau\; C_{lk}(\tau)e^{i\omega\tau} \quad (16)$$

237   Where

238
$$C_{kl}(\tau) = \tfrac{1}{2}\big(A_{kl}(\tau) + A_{kl}(-\tau)\big) \quad (17)$$

239   And

240
$$A_{kl}(\tau) = Tr_b\big(\rho^T U^k(\tau)U^l\big) = Tr_b\big(\rho^T U^k U^l(-\tau)\big) \quad (18)$$

241   The U operators are bath operators, the Tr_b is a partial trace over bath degrees of freedom with bath
242   equilibrium density matrix ρ^T, and the time dependence is that given by propagation by the bath
243   Hamiltonian. The index symmetries for the J's are then

244
$$J_{kl}(\omega) = J_{lk}(-\omega) = J_{-k-l}^*(-\omega) \quad (19)$$

245 We can now re-sum Hubbard's expression by way of the substitutions $l \rightarrow -l, s \rightarrow -s$ in the first term
246 and $k \rightarrow -k$ in the second and using

247
$$J_{-l}\left(\omega_{-s}^{-l}\right) = J_{l-k}^*(-\omega_{-s}^{-l}) = J_{l-k}^*(\omega_s^l) \qquad (20)$$

248 The commutators in Eq.(14) are then transformed into

249
$$[X^\dagger \sigma, V^k] + [(V^k)^\dagger, \sigma X] \qquad (21)$$

250 Where

251
$$X = \text{sech}(\beta\omega_s^l/2) J_{l-k}(\omega_s^l) O(\beta) V_s^l O(-\beta) \qquad (22)$$

252 We have transformed Hubbard's expression into Lindbladian form of the "non-Hermitian" type as
253 discussed in section 2. In doing so, the ease in demonstrating R(σ_{eq}) = 0 has been lost, but can be
254 restored by combining it with the alternative choice of substitutions $k \rightarrow -k$ in the first term and $l \rightarrow$
255 $-l, s \rightarrow -s$ in the second term, and averaging the two results.

256 Before reducing Eq.(22) further, an explication of Hubbard's operators is needed. As is common in NMR,
257 the interaction of spin and lattice degrees of freedom are decomposed into products, and indexed in the
258 same manner as Hubbard employs. Hermiticity is enforced by stipulating that operators with indices of
259 opposite sign are Hermitian conjugate to each other. The standard spherical tensor operators of rank L
260 and projection m, are of this type, and while Hubbard does not explicitly indicate this until examples are
261 offered at the end of his article, his V^k operators are basically spherical tensors, where Hubbard uses k to
262 denote the projection index m, and suppresses the rank index L. Likewise, Hubbard is not very explicit
263 regarding his V_s^l operators. He gives their desired properties, but not much on a *general* method for
264 their construction. The key idea is that of spectral decomposition (Halmos 1958) which produces an
265 operator expansion whose coefficients are the eigenvalues of the operator. For the Hamiltonian E we
266 have

267
$$E = \sum_i \omega_i E_i \qquad (23)$$

268 Where ω_i are the eigenvalues of *E* and the E_i are projection operators with the properties

269
$$E_i E_j = \delta_{ij} E_j ; \quad Tr(E_i E_j) = \delta_{ij} ; \quad \sum_i E_i = \mathbf{1} \qquad (24)$$

270 There are a number of methods for constructing the projectors. Perhaps the most straightforward is to
271 use the unitary matrix, U which brings the matrix E to diagonal form. With U at hand we have

272
$$E_i = U X^{ii} U^\dagger \qquad (25)$$

273 The fundamental basis matrices have elements $(X^{ij})_{\alpha\beta} = \delta_{i\alpha}\delta_{j\beta}$. A family of matrices can now be
274 constructed from a starting matrix V which will be "eigen-matrices" of the Hamiltonian propagator:

275
$$[E, E_i V E_j] = (\omega_i - \omega_j) E_i V E_j \qquad (26)$$

276
$$e^{iEt} E_i V E_j e^{-iEt} = e^{i(\omega_i - \omega_j)t} E_i V E_j \qquad (27)$$

277 When the V matrices are defined in the eigen-basis of E, this result is almost trivial, for in that case

$$(e^{iEt} V e^{-iEt})_{ij} = e^{i(\omega_i - \omega_j)t} V_{ij} \quad (28)$$

279 Even so, the use of projectors allows one to avoid writing out explicit matrix elements. Lexigraphical
280 ordering of these (i,j) index pairs can be adopted and assigned to indices that range from negative to
281 positive integers or odd half integers to obtain Hubbard's V^l_s and his frequencies ω^l_s. The original
282 mathematical lemmas and theorems of Gorini et.al heavily rely on the use of spectral decomposition.
283 Redfield's notation adopts the use of explicit matrix elements, and this perhaps is another of the reasons
284 for the popularity of his equations. Bengs and Levitt commence their own analysis by adopting an
285 eigenbasis for E as with Eq.(28). We can now also tie spectral decomposition to the factoring problem of
286 the previous section. If H is a positive matrix we can apply Eq.(25) to decompose H into a sum

$$H = \sum_k N_k N_k^\dagger \quad (29)$$

288 where the operators can be written in terms of the unitary matrix T which diagonalizes H with positive
289 eigenvalues λ_k as

$$N_k = \sqrt{\lambda_k} \, T \, X^{kk} \quad (30)$$

291 Returning to Hubbard's relaxation expression, one can use the properties of the V^l_s to evaluate the
292 effects of the operator O(β) on V^l_s by employing Eq. [27] with β replacing *it*. We can also expand V^k in
293 terms of V^l_s. Finally, we invoke the secular approximation, where rapidly oscillating terms, generated by
294 the evolution of E, are dropped. There are two paths that one can follow for this goal. One path takes
295 the Zeeman energy as dominant, and at high fields the spectral decomposition is not needed, since the
296 spherical tensor operators are already eigen-operators. The second assumes sufficient symmetry in the
297 bath statistics such that only $J_{l-l}(\omega^l_s)$ are nonzero, and then Hubbard's equation simplifies to

$$R(\sigma) = \sum_{ls} e^{\frac{\beta \omega^l_s}{2}} J_{l-l}(\omega^l_s) \operatorname{sech}(\beta \omega^l_s / 2) \{ [(V^l_s)^\dagger \sigma, V^l_s] - [\sigma V^l_s, (V^l_s)^\dagger] \} \quad (31)$$

299 In many situations, both conditions are applicable. The double sum in Eq.(29) is useful in zero field. In
300 either case, we have fully reduced Hubbard to Lindbladian form and essentially reproduced the main
301 result obtained by Bengs and Levitt by way of the Lindbladian formalism. One small difference is
302 Hubbard's use of the thermal symmetrizing factor given by the hyperbolic secant function. If so desired,
303 this can be removed as illustrated in Hubbard's paper. It is also imperative to emphasize the importance
304 of the secular approximation in obtaining the Lindblad form. Without this step, relaxation in the
305 rotating frame will be time dependent, with very different, and perhaps even unphysical dynamics. This
306 same approximation is required in a Lindbladian approach, which is often referred to as the "rotating
307 frame" approximation (Manzano 2020).

308 While very compact, the presence of a finite temperature steady state is definitely obscure. From
309 Eq.(29) directly, the only apparent recourse is to expand the dynamics in a complete set of basis
310 matrices and search for one or more zero eigenvalues. Such a procedure is illustrated in an example
311 with a simple two dimensional density matrix dynamics in (Manzano 2020) where eigenvalues are easily
312 computed. This is in contrast to Hubbard's original expression, Eq.(14), where the steady state is clearly

313   recognizable, even for arbitrarily large dimensions. Alternatively, we can invoke the secular
314   approximation directly to Eq.(14) and we can enjoy a compromise where one retains the clear presence
315   of the steady state. Hubbard teaches us how to retain explicit information on the fixed point density
316   matrix. However, this seems to be possible only when dynamic frequency shifts can be ignored.

317   One should also appreciate that a homogeneous system which possess a zero eigenvalue is closely
318   related to an inhomogeneous system. The procedure of homogenizing an inhomogeneous system by
319   incorporating the inhomogeneous vector into equations with an additional dimension, which is invariant
320   with an eigenvalue of zero, has been employed in a Bloch equation analysis of spin echoes (Bain 2011) ,
321   steady state precession (Nararova 2004) and relaxation (Levitt 1992) . Going in the opposite direction
322   can be considerably more difficult.

323   4. **Bloch and Hubbard and Rotating Frame Relaxation:**

324   We now take a side turn to another aspect of the pioneering work of Bloch and Hubbard, which also has
325   largely gone unrecognized in the NMR literature. As explained in the introduction, the author was
326   recently reacquainted with these aspects in an effort to go beyond a Bloch equation picture with only R_1
327   and R_2 for spin locks and adiabatic sweeps in the presence of exchange (Barbara 2016). Both examples
328   illustrate the use of the high temperature, weak ordering situation that occurs when the full theory
329   contained in Eq.(29) is reduced to the appropriate limit for those circumstances. These applications do
330   not require the Lindbladian form. Nevertheless, it strikes the author as a wasted opportunity to not
331   mention the treatment of rotating frame relaxation by Bloch and Hubbard and therefore reintroduce
332   these two results to 21st century NMR scientists.

333   At the end of Bloch's paper, he applies his theory to relaxation in the presence of an RF field. For a rank
334   one tensor interaction, such as the fluctuating field relaxation mechanism, he derives a set of
335   generalized Bloch equations in the *rotating frame:*

336
$$\begin{pmatrix} \dot{M}_x \\ \dot{M}_y \\ \dot{M}_z \end{pmatrix} + \begin{pmatrix} A_x & -\Omega\cos(\theta) & a_x \\ \Omega\sin(\theta) & A_y & -\Omega\sin(\theta) \\ a_z & \Omega\sin(\theta) & A_z \end{pmatrix} \begin{pmatrix} M_x \\ M_y \\ M_z \end{pmatrix} = \begin{pmatrix} c_x \\ 0 \\ c_z \end{pmatrix} \quad (32)$$

337   When the Rabi frequency, $\Omega\sin(\theta)$ is much smaller than the Larmor frequency ω_0, but still comparable
338   to the resonance offset, $\Omega\cos(\theta)$, we have $a_z = c_x = 0$. At high temperature, $c_z = R_1 M_0$ as usual. In terms
339   of the spectral densities, $J_n(\omega)$ the relaxation parameters are given by the equations

340
$$A_x = A_y = J_1(\omega_0) + J_0(\Omega) + \big(J_0(0) - J_0(\Omega)\big)\cos^2(\theta) \quad (33)$$

341
$$A_z = 2J_1(\omega_0) \quad (33)$$

342
$$a_x = -\big(J_0(0) - J_0(\Omega)\big)\sin(\theta)\cos(\theta) \quad (34)$$

343   In the absence of an RF field, $\theta=0$ and A_x and A_z are R_2 and R_1 respectively. Note that a_x is generally not
344   zero if the locking field is off resonance.

345   It is not always appreciated that the usual formulas for rotating frame relaxation are those for the case
346   when the locking field, whose magnitude is given by Ω, is much larger that the relaxation rates. In that
347   situation, a first order perturbation is applicable (Barbara 2016). If the transformation, denoted by V,
348   diagonalizes the Bloch equations without relaxation, the first order contribution from the relaxation

349 matrix elements is given by the diagonal elements of $V^{-1}RV$, which are then rotating frame relaxation
350 rate constants:

$$\rho_1 = R_1 cos^2(\theta) + \left(R_2 - \left(J_0(0) - J_0(\Omega)\right)\right)sin^2(\theta) \quad (35)$$

$$\rho_2 = \frac{1}{2}R_2 + \frac{1}{2}\left(R_2 cos^2(\theta) + \left(R_1 + J_0(\Omega) - J_0(0)\right)sin^2(\theta)\right) \quad (36)$$

353 When the low frequency terms are collected, one obtains expressions that reproduce those for chemical
354 shift exchange, as usually derived from an analysis of exchange perturbation in the limit of fast exchange
355 using the Bloch-McConnell equations (Barbara 2016), (Abergel 2003). This result is often attributed to
356 (Wennerstrom 1972). The theory was already presented in Bloch's paper in 1957. Uncorrelated local
357 fields for two spin ½ systems is an important mechanism for spin isomer conversion, as discussed in
358 Bengs and Levitt.

359 Bloch presents other applications to his formalism that are of interest. These applications offer an
360 excellent catalytic motivation for going through many of his notational details.

361 After his own exposition and refinement of Bloch's theory, Hubbard also gives an application to rotating
362 frame relaxation, and ups the ante, by considering second rank, dipole-dipole relaxation mechanisms.
363 Hubbard obtains equations for the magnetization dynamics similar to Eq.[32] , with off diagonal
364 contributions. After taking the first order contribution, the rotating frame, spin lattice rate constant is
365 given by

$$\rho_1 = R_1 cos^2(\theta) + R_2 sin^2(\theta) - 6sin^2(\theta)\{-J_0(0) + cos^2(\theta)J_0(\Omega) + sin^2(\theta)J_0(2\Omega)\} \quad (37)$$

367 In terms of the spectral densities, R_1 and R_2 are

$$R_1 = 4\left(J_1(\omega_0) + 4J_2(2\omega_0)\right) \quad (38)$$

$$R_2 = 6J_0(0) + 10J_1(\omega_0) + 4J_2(2\omega_0) \quad (39)$$

370 This result was produced in very different notation in (Blicharski 1972). Unfortunately, in that work, the
371 various contributions are gathered together in such a manner as to obscure the origin of, and the
372 relationship to each. The reader should keep in mind that for both examples, details regarding scale
373 factors of the spectral densities have been suppressed. These can be added according to the specific
374 needs of their application, be it dipolar, quadrupolar, fluctuating field, or chemical shift exchange.

375 5. Comments and Conclusions:

376 Given the maturity of the topic of relaxation in magnetic resonance, it is not often that a surprise is
377 forthcoming. Many modern treatments, that are very application oriented, reflect this maturity. For
378 example, the extensive overview offered by Kowalewski and Maler (Kowalewski 2007) details many of
379 the modern applications. Bloch is not listed in the index, and Hubbard is indexed only in the context of
380 work he did on rotational diffusion applications and the calculation of correlation functions, even
381 though reference Hubbard's review article is cited in the chapter titled *Redfield Relaxation Theory*. In
382 Redfield's later effort, which appeared as a chapter in *Advances in Magnetic Resonance* (Redfield 1965),
383 Redfield acknowledges the influence of Bloch, and offers his own equations that account for relaxation
384 at finite temperatures, while only citing Hubbard's review article in passing. Redfield makes no effort to
385 demonstrate or expound on the relationship between his expression, and Bloch's or Hubbard's. A

386   glance at Redfield's equation 3.15 in (Redfield 1965) induces one to question in what way his result is
387   also Lindbladian, for the expression is very different than Hubbard's equation Eq.(100). The factoring of
388   the spectral densities that Hubbard achieves does not rely on the secular approximation. Nonetheless, a
389   careful study reveals that Redfield's equation is also a mixed Lindbladian type, similar to Eq.(21-22).
390   Here one can fully appreciate the power of using spectral decomposition to factor out the spectral
391   densities, and in doing so, produce an expansion in non-Hermitian operators. Redfield's 1965 result,
392   which *is based on a Hermitian operator expansion* and looks nothing like a Lindbladian, is nonetheless as
393   serviceable as Hubbard's.

394   Approaches to NMR relaxation theory have changed over its history. In the work of Bloch, Redfield and
395   Hubbard, extensive manipulations are carried out at the level of second order perturbation theory for
396   the *solutions* to the interaction representation density matrix. After extensive manipulations, a finite
397   time step expression is produced, which is argued to be basically the solution to a given differential
398   equation. However, already in the same year that Hubbard's review article appeared in print, Abragam
399   took the alternative approach by directly iterating the differential equation in his treatment of
400   relaxation (Abragam 1983). This is now the usual practice, and is the path taken, for example, by
401   Goldman in his review of NMR relaxation theory (Goldman 2000), who offers his own treatment of a
402   finite temperature relaxation theory therein and also uses spectral decomposition for that case. This
403   same iteration approach is also adopted by recent expositions using the Lindbladian formalism and weak
404   collision, Markovian bath dynamics and the secular approximation. Again, a good illustration of this is
405   given in Manzano. As mentioned earlier, a study of that overview reveals that many of the same tools,
406   e.g. use of Hamiltonian projection operators to obtain eigen-matrices, as used by Bloch and Hubbard,
407   are also brought to bear in the same manner. The historical overview mentioned in section 2
408   (Chruscinski 2017), also outlines other open quantum system efforts made by various researchers, and
409   there is a strong enough similarity to suspect that these have rediscovered the main results of Bloch and
410   Hubbard, as well as having anticipated the Lindbladian form.

411   It is possible to make the argument that NMR theory needs to modernize, in keeping with new
412   approaches that appear to have a more firm foundation in quantum theory. The author is reminded of a
413   classic collection of essays (Peierls 1979) with the surprise here, that these new methods can find their
414   own perfect reflection in the best work of the old masters.

415

416   Appendix: Some Elaborations on Lindblad and Section 2.

417   In this appendix, a *sketch* of further aspects of the Lindbladian form is offered. It is self-contained and
418   does not require further references than those already provided.

419   The most general transformation for a matrix, in particular the density matrix can be written in the form

420
$$\rho' = \sum_{\alpha\beta'\beta'} C_{\alpha\beta\alpha'\beta'} \, X^{\alpha\beta} \rho X^{\alpha'\beta'} \qquad (A1)$$

421   Where the $X^{\alpha\beta}$ are the fundamental basis matrices defined in Section 3. Rather than derive this
422   equation, one can grasp that it is correct by reducing it to component form

13

423
$$\rho_{ij}{}' = \sum_{\beta\alpha'} C_{i\beta\alpha'j}\ \rho_{\beta\alpha'} \qquad (A2)$$

424 Here, one recognizes the Redfield notation but with slightly rearranged indices. Introducing a complete
425 set of Hermitian matrices O_k provides for a more compact notation where now

426
$$\rho' = \sum_{kk'} G_{kk'}\ O_k \rho O_{k'} \qquad (A3)$$

427 If the transformation preserves the Hermitian character of the density matrix, G is Hermitian in the k
428 indices $G_{kk'} = G_{k'k}{}^*$. If the trace is also invariant we have

429
$$\sum_{kk'} G_{kk'}\ O_{k'} O_k = \mathbf{1} \qquad (A4)$$

430 This is now all we need to obtain a difference equation in $\rho' - \rho$ and obtain the Lindblad form. However
431 this is not usually the way the problem is approached. Instead the starting point is from the "Kraus
432 form", which is obtained by assuming that the matrix G is positive. Being positive, one can factor G in
433 the same manner illustrated in Section 3 via the spectral decomposition for H. This then allows
434 summations over the k indices to produce the Kraus operators for the transformation. The one
435 remaining index is over the eigenvalue index. However this is basically going a step to far, and it is more
436 direct to use Eq.(A3). The required subtraction can be implemented by substituting Eq.(A4) for the
437 identity in a symmetrical manner:

438
$$\rho' - \rho = \sum_{kk'} G_{kk'}\ O_k \rho O_{k'}\ -\tfrac{1}{2}(\rho\mathbf{1} + \mathbf{1}\rho) \qquad (A5)$$

439 To complete the process, one now extracts those terms in the operator expansion that involves the
440 identity operator, which we ascribe to the zero index $O_0 = \mathbf{1}.$ It is a simple matter to see that these can
441 be collected into the expression

442
$$\sum_{k} \tfrac{1}{2i}\ (G_{k0} - G_{k0}{}^*)\ i[O_k, \rho] \qquad (A6)$$

443 This represents the part of the transformation generated by a commutator. The remaining part, where
444 the sums now exclude the identity matrix, is now of the Lindbladian form

445
$$\rho' - \rho = \sum_{kk'} G_{kk'} \left[O_k \rho O_{k'} - \tfrac{1}{2}\{\rho,\ O_{k'}O_k\} \right] \qquad (A7)$$

446 One can then use the positivity of G to factor this expression into non-Hermitian operators. In this way
447 one can see that the approaches from the generalized differential equation and the one based on the
448 general solution are equivalent.

449

450

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