The Lindbladian Form

And

The Reincarnation of Felix Bloch's Generalized Theory of Relaxation

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16   Abstract

17

18   The relationship between the classic magnetic resonance density matrix relaxation theories of Bloch and
19   Hubbard, and the modern Lindbladian master equation methods are explored.   These classic theories
20   are in full agreement with the latest results obtained by the modern methods. A careful scrutiny shows
21   that this also holds true for Redfield's later treatment, offered in 1965. The early contributions of Bloch
22   and Hubbard to rotating frame relaxation theory are also highlighted. Taken together, these seminal
23   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.

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

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

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

84

85 **2: A Guide to Lindblad**

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

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

106
$$\dot{c}_\iota = \sum_j M_{ij}\, c_j \qquad (1)$$

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

110
$$\varrho_{ij} = c_i c_j^* \qquad (2)$$

111 The square of all rank-one matrices are proportional to themselves, $\varrho^2 = \alpha\varrho$, so that in this case $\alpha =$
112 $\Sigma c_i c_i^*$. However, keep in mind that the converse does not hold true. The terminology of "rank" has a
113 number of variants, and in this section we adopt the usage common in the theory of matrices (Halmos
114 1958).

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

117
$$\dot{\varrho} = M\varrho + \varrho M^\dagger \qquad (3)$$

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

119
$$\varrho(t) = \Upsilon(t)\varrho(0)\Upsilon(t)^\dagger; \;\; \dot{\Upsilon}(t) = M\Upsilon(t); \;\; \Upsilon(0) = 1 \qquad (4)$$

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

126
$$M = -\frac{1}{2}H + A \qquad (5)$$

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

130
$$\dot{\varrho} = -\frac{1}{2}\{H, \varrho\} + [A, \varrho] \qquad (6)$$

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

135
$$\dot{\varrho} = -\frac{1}{2}\{NN^\dagger, \varrho\} + [A, \varrho] + N^\dagger\varrho N \qquad (7)$$

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

140   Kronecker product of the matrix with the identity matrix of arbitrary dimension also be positive
141   (Manzano 2020). This condition has been essential for a strict mathematical proof and also ensures that
142   the density matrix has real, positive eigenvalues. Complete positivity has been critiqued in (Pechukas
143   1994) and (Shaji 2005).

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

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

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

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

164
$$\left[N, \varrho N^\dagger\right] + \left[N\varrho, N^\dagger\right] = -\left\{N^\dagger N, \varrho\right\} + 2N\varrho N^\dagger \qquad (8)$$

165   In this equation, the alternative factoring, $H = N^\dagger N$ has been adopted. If N is a normal
166   matrix, $[N^\dagger, N] = 0$, the ordering is not important, and in this case, the identity matrix, which
167   corresponds to an infinite temperature limit to within a scalar factor, is a steady state. A similar
168   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
169   Hermitian. The resulting expression can be written in terms of nested commutators:

170
$$\left[[H_1, \varrho], H_2\right] + \left[[H_2, \varrho], H_1\right] \qquad (9)$$

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

173
$$\left[S\varrho, S^\dagger\right] + [S, \varrho S^\dagger] - \left(\left[D\varrho, D^\dagger\right] + [D, \varrho D^\dagger]\right) \qquad (10)$$

174   Even though *S* and *D* are both Hermitian, Hermitian conjugates have been kept explicit in order to
175   conform with Eq.[8]. One simple method for constructing a non-normal factoring is to insert the identity
176   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
177   course, Q must be Hermitian in order to preserve the Hermitian character of the density matrix in Eq.(7).

178   Non-normal expansions are also generated quite naturally when spectral decomposition is employed.
179   That procedure will be treated in the next section when the operator expansions of Bloch and Hubbard
180   are discussed.

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

184
$$k(R\varrho R - \varrho) \qquad (11)$$

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

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

192
$$\dot{\varrho} = AB^\dagger \varrho + \varrho BA^\dagger - A^\dagger \varrho B - B^\dagger \varrho A \qquad (12)$$

193   Or

194
$$\dot{\varrho} = -\{[B^\dagger \varrho, A] + [A^\dagger, \varrho B]\} \qquad (13)$$

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

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

202   Whereas this guide to Lindblad should be sufficient for practical purposes, the perspective from a
203   differential approach may not be satisfactory for some readers, perhaps even confusing given the
204   heuristic nature of the construction. Therefore, an outline of the approach from the general solution
205   perspective is offered in the appendix.

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

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

214 As announced in the introduction, is not the author's goal to give an in depth review of the Bloch-
215 Hubbard theory. In particular, Hubbard's exposition is especially clear on most accounts, and those with
216 sufficient interest can directly consult the original publications. Rather, the intention is to provide
217 reasons and the motivation for others to read or revisit these classic works. It is useful to point out here
218 at the outset that many of the mathematical methods used with modern Lindbladian approaches to
219 Markovian systems are exactly those used by Bloch and Hubbard, and other aspects of this fact will be
220 emphasized in the conclusions. Since the success of the Bloch-Hubbard theory has gone unrecognized
221 for so many years, and has now been brought into the limelight by the work of Bengs and Levitt, a
222 demonstration of the equivalence can be considered an original contribution to the topic.

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

224 $$R(\sigma) = \sum_{kls} \text{sech}(\beta\omega_s^l/2) J_{lk}(\omega_s^l)\{[O(-\beta)V_s^l O(\beta)\,\sigma, V^k] - [\sigma\,O(\beta)V_s^l O(-\beta), V^k]\} \qquad (14)$$

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

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

235 $$(V_s^l)^\dagger = V_{-s}^{-l}; \quad \omega_{-s}^{-l} = -\omega_s^l; \quad V^l = \sum_s V_s^l \qquad (15)$$

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

239 $$J_{lk}(\omega) = \frac{1}{2}\int_{-\infty}^{\infty} d\tau\, C_{lk}(\tau)e^{i\omega\tau} \qquad (16)$$

240 Where

241 $$C_{kl}(\tau) = \tfrac{1}{2}\big(A_{kl}(\tau) + A_{kl}(-\tau)\big) \qquad (17)$$

242 And

243 $$A_{kl}(\tau) = Tr_b\big(\rho^T U^k(\tau)U^l\big) = Tr_b\big(\rho^T U^k U^l(-\tau)\big) \qquad (18)$$

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

247
$$J_{kl}(\omega) = J_{lk}(-\omega) = J^*_{-k-l}(-\omega) \qquad (19)$$

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

250
$$J_{-l}\left(\omega^{-l}_{-s}\right) = J^*_{l-k}\left(-\omega^{-l}_{-s}\right) = J^*_{l-k}\left(\omega^l_s\right) \qquad (20)$$

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

252
$$\left[X^{\dagger}\sigma, V^k\right] + \left[\left(V^k\right)^{\dagger}, \sigma X\right] \qquad (21)$$

253 Where

254
$$X = \text{sech}\left(\beta\omega^l_s/2\right)J_{l-k}\left(\omega^l_s\right)O(\beta)V^l_sO(-\beta) \qquad (22)$$

255 We have transformed Hubbard's expression into Lindbladian form of the "non-Hermitian" type as
256 discussed in section 2. In doing so, the ease in demonstrating R(σ_{eq}) = 0 has been lost, but can be
257 restored by combining it with the alternative choice of substitutions $k \to -k$ in the first term and $l \to$
258 $-l, s \to -s$ in the second term, and averaging the two results.

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

270
$$E = \sum_i \omega_i E_i \qquad (23)$$

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

272
$$E_i E_j = \delta_{ij} E_j ; \quad Tr\left(E_i E_j\right) = \delta_{ij} ; \quad \sum_i E_i = \mathbf{1} \qquad (24)$$

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

275
$$E_i = UX^{ii}U^{\dagger} \qquad (25)$$

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

278
$$\left[E, E_i V E_j\right] = \left(\omega_i - \omega_j\right)E_i V E_j \qquad (26)$$

279
$$e^{iEt} E_i V E_j e^{-iEt} = e^{i(\omega_i - \omega_j)t} E_i V E_j \qquad (27)$$

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

281
$$(e^{iEt} V e^{-iEt})_{ij} = e^{i(\omega_i - \omega_j)t} V_{ij} \qquad (28)$$

282 Even so, the use of projectors allows one to avoid writing out explicit matrix elements. Lexigraphical
283 ordering of these (i,j) index pairs can be adopted and assigned to indices that range from negative to
284 positive integers or odd half integers to obtain Hubbard's V^l_s and his frequencies ω^l_s. The original
285 mathematical lemmas and theorems of Gorini et.al heavily rely on the use of spectral decomposition.
286 Redfield's notation adopts the use of explicit matrix elements, and this perhaps is another of the reasons
287 for the popularity of his equations. Bengs and Levitt commence their own analysis by adopting an
288 eigenbasis for E as with Eq.(28). We can now also tie spectral decomposition to the factoring problem of
289 the previous section. If H is a positive matrix we can apply Eq.(23) to decompose H into a sum

290
$$H = \sum_k N_k N_k^\dagger \qquad (29)$$

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

293
$$N_k = \sqrt{\lambda_k} \, T \, X^{kk} \qquad (30)$$

294 Returning to Hubbard's relaxation expression, one can use the properties of the V^l_s to evaluate the
295 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
296 terms of V^l_s. Finally, we invoke the secular approximation, where rapidly oscillating terms, generated by
297 the evolution of E, are dropped. If the Zeeman energy as dominant, the spectral decomposition is not
298 needed, since the spherical tensor operators are already eigen-operators. A single sum over the V^l
299 terms remain. Otherwise one needs sums over both l and s:

300
$$R(\sigma) = \sum_{ls} e^{\frac{\beta \omega^l_s}{2}} J_{l-l}(\omega^l_s) \, \text{sech}(\beta \omega^l_s / 2) \left\{ \left[(V^l_s)^\dagger \sigma, V^l_s \right] - \left[\sigma V^l_s, (V^l_s)^\dagger \right] \right\} \qquad (31)$$

301 The double sum in Eq.(31) is useful in zero field. We have now fully reduced Hubbard to Lindbladian
302 form and essentially reproduced the main result obtained by Bengs and Levitt by way of the Lindbladian
303 formalism. One small difference is Hubbard's use of the thermal symmetrizing factor given by the
304 hyperbolic secant function. If so desired, this can be removed as illustrated in Hubbard's paper. It is
305 also imperative to emphasize the importance of the secular approximation in obtaining the Lindblad
306 form. Without this step, relaxation in the rotating frame will be time dependent, with very different,
307 and perhaps even unphysical dynamics. This same approximation is required in a Lindbladian approach,
308 which is often referred to as the "rotating wave" approximation (Manzano 2020).

309 While very compact, the presence of a finite temperature steady state is definitely obscure. From
310 Eq.(31) directly, the only apparent recourse is to expand the dynamics in a complete set of basis
311 matrices and search for one or more zero eigenvalues. Such a procedure is illustrated in an example
312 with a simple two dimensional density matrix dynamics in (Manzano 2020) where eigenvalues are easily
313 computed. This is in contrast to Hubbard's original expression, Eq.(14), where the steady state is clearly
314 recognizable, even for arbitrarily large dimensions. Alternatively, we can invoke the secular

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

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

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

325 We now take a side turn to another aspect of the pioneering work of Bloch and Hubbard, which also has
326 largely gone unrecognized in the NMR literature. As explained in the introduction, the author was
327 recently reacquainted with these aspects in an effort to go beyond a Bloch equation picture with only R_1
328 and R_2 for spin locks and adiabatic sweeps in the presence of exchange (Barbara 2016). Both examples
329 illustrate the use of the high temperature, weak ordering situation that occurs when the full theory
330 contained in Eq.(31) is reduced to the appropriate limit for those circumstances. These applications do
331 not require the Lindbladian form. Nevertheless, it strikes the author as a wasted opportunity to not
332 mention the treatment of rotating frame relaxation by Bloch and Hubbard and therefore reintroduce
333 these two results to 21st century NMR scientists.

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

337
$$\begin{pmatrix} \dot{M}_x \\ \dot{M}_y \\ \dot{M}_z \end{pmatrix} + \begin{pmatrix} A_x & -\Omega\cos(\theta) & a_x \\ \Omega\sin(\theta) & A_y & -\Omega\sin(\theta) \\ a_z & \Omega\sin(\theta) & A_z \end{pmatrix} \begin{pmatrix} M_x \\ M_y \\ M_z \end{pmatrix} = \begin{pmatrix} c_x \\ 0 \\ c_z \end{pmatrix} \quad (32)$$

338 When the Rabi frequency, $\Omega\sin(\theta)$ is much smaller than the Larmor frequency ω_0, but still comparable
339 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
340 of the spectral densities, $J_n(\omega)$ the relaxation parameters are given by the equations

341
$$A_x = A_y = J_1(\omega_0) + J_0(\Omega) + \big(J_0(0) - J_0(\Omega)\big)cos^2(\theta) \qquad (33)$$

342
$$A_z = 2J_1(\omega_0) \qquad (33)$$

343
$$a_x = -\big(J_0(0) - J_0(\Omega)\big)\sin(\theta)\cos(\theta) \qquad (34)$$

344 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
345 zero if the locking field is off resonance.

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

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

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

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

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

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

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

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

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

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

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

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

376 **5. Comments and Conclusions:**

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

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

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

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

416

417   Appendix: Some Elaborations on Lindblad and Section 2.

418   In this appendix, a *sketch* of further aspects of the Lindbladian form is offered. It is self-contained and
419   does not invoke the various mathematical theorems often used as a starting point (Manzano 2020).

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

454

458

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