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Controllability of molecular systems

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In this paper we analyze the controllability of quantum systems arising in molecular dynamics. We model these systems as systems with finite numbers of levels, and examine their controllability. To do this we pass to their unitary generators and use results on the controllability of invariant systems on Lie groups. Examples of molecular systems, modeled as finite-dimensional control systems, are provided. A simple algorithm to detect the controllability of a molecular system is provided. Finally, we apply this algorithm to a five-level system.

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I. INTRODUCTION

Recent advances in laser technology has opened up the possibility of actively controlling molecular systems in the quantum regime. Prompted by this possibility, researchers initially advocated several schemes that were largely based on physical intuition. The severe limitations of such techniques later gave rise to investigations that made systematic use of optimal control theory. The current status of experimental and theoretical studies in the coherent control of phenomena at the quantum level is extensively surveyed in [1]. The text [2] also has several detailed examples of control at the quantum level.

A very natural question which arises out of the aforementioned investigations is the following. Which states can be achieved via the use of an external field (or an artificially imposed potential)? If nothing else, an answer to this question provides a means of testing the feasibility of a putative experiment. Such a study can proceed at several levels. For instance, one may view Schrödinger's equation with an external field as an infinite-dimensional bilinear system and then investigate its controllability. This was carried out in [3]. Alternatively, one may express Schrödinger's equations with respect to a finite number of eigenstates of an operator of interest (usually the internal Hamiltonian) and obtain, thereby, a finite-dimensional bilinear control system and proceed to study its controllability. This approach will be the subject of this paper, with special attention being paid to molecular systems. We will compare our work, briefly, with that of [3] in Sec. VI of the paper. One can further classify the analysis of controllability by addressing the same issue under some restrictions on the nature of the external control. For instance, one can restrict the amplitude of the external last field to a suitable upper bound (which may embody laboratory restrictions, for instance). We will also incorporate similar stipulations on the external control in our analysis, where possible.

To illustrate the ideas behind the concept of controllability on a context familiar to researchers in molecular dynamics, we consider the usual quantum-mechanical system described by Schrödinger's equation:

$$i\hbar\dot{\psi}=(H_0+H_I)\psi, \quad \psi(0)=\psi_0 . \tag{1}$$

H_0 refers to the unperturbed (internal) Hamiltonian and H_I is the interaction (external) Hamiltonian. Suppose the system is initially in state $\psi(0)=\psi_0$, and the intention is to force the system to state ψ_d at some time T. Then the question of controllability is to find, if possible, H_I and T so that $\psi(T)=\psi_d$. H_I could come in one of many forms. In applications to laser-driven processes it is usually the dot product of the electric dipole and the external laser field. Since the dipole gradient is fixed, one can only vary the external field. Another example arises in solid-state physics where H_I is an external, time-independent, spatial potential which is to be artificially constructed to achieve the final state of interest [4]. In this paper we will focus on the situation where the interaction Hamiltonian is time varying. The analysis for the time-independent case, though similar in favor, apparently does not lead to any easily stated criterion for controllability.

The balance of the paper will be organized as follows: first we will demonstrate how certain quantum-mechanical systems may be modeled, either approximately or exactly, as invariant systems on finite-dimensional groups of unitary matrices (see Sec. II for a definition of the same); next we will present results concerning the controllability of invariant systems on Lie groups. We will then apply these results to molecular systems described by a quantum model with a finite number of levels (finite-level model), in particular to a five-level system taken from [5]. In Sec. VI we will justify the use of finite-level models and then draw some conclusions about the utility of the circle of ideas introduced earlier in the paper.

II. INVARIANT SYSTEMS ON UNITARY GROUPS AND QUANTUM SYSTEMS

Let us write Schrödinger's equation with an external interaction Hamiltonian, with respect to an eigenbasis of some operator of interest. Accordingly, if $\psi(x,t) = \sum_n a_n(t)\psi_n(x)$ is the decomposition of the state of the quantum-mechanical system, then after a truncation to a finite number N of eigenstates of interest, Schrödinger's equation leads to the following equation:

$$\dot{\mathbf{a}} = A\mathbf{a} + C\mathbf{a} \ , \tag{2}$$

where $\mathbf{a}$ stands for $(a_1(t), \ldots, a_N(t))^t$; and A and C stand for the matrix representation of the internal and interaction Hamiltonians divided by the numerical constant $i\hbar$, respectively. Thus, in particular, A and C are $N\times N$ skew-Hermitian matrices. In solid-state applications one seeks to find a potential $V(x)$ with matrix representation C. In molecular applications $C = B\epsilon(t)$, where B is the matrix representation of the dipole operator, and $\epsilon(t)$ is the external laser field. From this point onwards we will only consider, unless explicitly specified to the contrary, the application to molecular problems.

Associated with (2) is the equation which describes the time evolution of the corresponding unitary generator:

$$\dot{U}(t) = AU(t) + \epsilon(t)BU(t) \ . \tag{3}$$

System (3) is again a control system, whose "state" (in the control-theoretic sense) is the unitary generator $U(t)$. For studying the controllability properties of (2), it is convenient to study the controllability properties of (3). This relation stems from the following fact. The state of (2), namely $\mathbf{a}$, being a probability amplitude lies on the $(2N-1)$-dimensional unit sphere. Now, one can show that given any two points on the $(2N-1)$-dimensional sphere there is always a unitary $N\times N$ matrix which acts on one to give the other. One can explicitly construct all the unitary matrices which have this property. Therefore, to show that a certain final vector on the $(2N-1)$-sphere can be obtained at some final time starting from some given initial vector on the same sphere, it suffices to show that the unitary matrix taking the former to the latter can be obtained at that final time, given that the initial condition was the identity matrix. Therefore, the study of the controllability properties of system (3) gives useful information concerning the controllability properties of system (2). This is crucial because system (3) is an example of an invariant system on a compact Lie group, and as we will see in Sec. III these are nonlinear control systems whose controllability can be analyzed via a simple algebraic criterion, whereas the controllability analysis of system (2) does not lend itself to any criterion of comparable simplicity.

To describe more precisely an invariant system we first need several definitions. All the definitions that we will introduce in this section could be stated in far greater generality. We will state them only in a fashion adapted to our requirements. We first begin with the definition of a Lie algebra.

Definition 2.1. A Lie algebra h of matrices is a subspace of the vector space of $n\times n$ matrices with complex entries which is stable under the Lie bracket operation; i.e., if we define the Lie bracket of two matrices A and B, which belong to h, to be the matrix AB-BA denoted as $[A,B]$, then $[A,B]$ also belongs to h.

In the definition of a Lie algebras above, it is to be understood that the field, over which the vector space structure of h is defined, is the field of real numbers R. In particular, when we speak of the dimension of h we mean its dimension over the field of real numbers; i.e., to demonstrate that the dimension of h is some number K, it suffices to exhibit K members of h, $h_1, \ldots, h_K$, so that every member of h may be written as a linear combination, with *real* coefficients, of $h_1, \ldots, h_K$.

There are two examples of Lie algebras of importance to our situation. The first is the Lie algebra of $N\times N$ skew-Hermitian matrices denoted by u(N). That it is a Lie algebra of dimension N^2 is easy to ascertain. The second Lie algebra of interest to us is su(N), the Lie algebra of $N\times N$ zero-trace, skew-Hermitian matrices, and its dimension is N^2-1.

Definition 2.2. Given a Lie algebra h of matrices we define the connected Lie group associated with h to be the set of all finite products of matrices, where each factor in these products is the matrix exponential of any matrix in h. Furthermore, the dimension of the Lie group associated with h is the same as that of h.

The Lie group associated with u(N) is the Lie group of $N\times N$ unitary matrices, while that associated to su(N) is the Lie group of $N\times N$ special unitary matrices. The notation for these two Lie groups is U(N) and SU(N), respectively.

Definition 2.3. An invariant system on the Lie group G, where G is the Lie group associated with a Lie algebra h, is a control system defined by the equations:

$$\dot{U} = AU(t) + \sum_{i=1}^{m} u_i(t)B_iU(t) \ , \tag{4}$$

where A and the $B_i, i=1,\ldots,m$ belong to h; $U(t)$ belongs to G, and $u_i(t)$ are scalar functions of time which play the role of the external control.

Thus, in particular Eq. (3) defines an invariant system on U(N).

Remark 2.1. Both the unitary group and the special unitary group are compact Lie groups. We will not define a compact Lie group here, but we will mention that compactness of a Lie group can be ascertained by an algebraic test. The test consists of computing the Killing form (see [6,7]) of the Lie algebra of the Lie group in question and determining if it is negative definite.

We will end this brief introduction to Lie groups with a simple result which will be of use later.

Proposition 2.1. Any unitary matrix U satisfies $U=e^{i\gamma}V$, where γ is a real number and V is a special unitary matrix.

Proof. U, being unitary can be written as e^{iS} for some Hermitian matrix S. Let γ be the trace of S. γ is a real number since S, being Hermitian, has all its eigenvalues real. Define a matrix T by $T=S-\gamma I_{n\times n}$, where $I_{n\times n}$ stands for the identity matrix of n rows and n columns (n, being the order of the matrix U). T is also Hermitian and has trace 0. Hence the matrix e^{iT} is special unitary. We denote this special unitary matrix by V. Now $U=e^{iS}=e^{i(T+\gamma I_{n\times n})}=e^{i\gamma}e^{iT}$. The last equality stems from the commutativity of T and the identity matrix.

We will, in concluding this section, present two examples of control systems which are closely related to the theme of the paper.

Example. We consider the control of a spin-$\frac{1}{2}$ particle in an external magnetic field B, with components B_x, B_y, and B_z. The dynamics of this system are given by Schrödinger's equation, with the Hamiltonian of the system being

$$H=\mu(B_x\sigma_x+B_y\sigma_y+B_z\sigma_z)$$

where the σ's are the familiar Pauli matrices which are zero-trace, Hermitian matrices, and μ is the magnetic moment. The external controls for this system are, of course, the components of the magnetic field B and, hence, there are three controls. This is an example of an invariant system on SU(2) obtained, not via truncation, but exactly as there are only two possible values that the spin of the particle can assume, namely $+\frac{1}{2}$ and $-\frac{1}{2}$.

Example. Coupled harmonic oscillator: Let q and p denote the vectors of expectation values of the conjugate positions and momenta, and let $H_0=\frac{1}{2}p^TGp+\frac{1}{2}q^TFq$, $H_I=-B^Tqu$ be the internal and external Hamiltonian, respectively. In the above, G is the inverse of the mass matrix and F is the force constant matrix. By virtue of Ehrenfest's theorem, the corresponding control system can be described by

$$\frac{d}{dt}\begin{bmatrix} q \\ p \end{bmatrix}=\begin{bmatrix} G_p \\ -Fq \end{bmatrix}+\begin{bmatrix} 0 \\ B \end{bmatrix}u .$$

The controllability of the above system can be determined using the famous Kalman rank condition, according to which the control system, obtained above, is controllable if

$$\operatorname{rank}\,[\hat{B}\hat{A}\hat{B}\cdots A^{2\hat{n}-1}\hat{B}]=2n ,$$

where the matrices $\hat{A}$ and $\hat{B}$ are given by

$$\hat{A}=\begin{bmatrix} 0 & G \\ -F & 0 \end{bmatrix}$$

and

$$\hat{B}=\begin{bmatrix} 0 \\ B \end{bmatrix} .$$

This follows from the fact that the dimension of the state space of this linear control system, which is the usual phase space of classical mechanics, is $2n$ (in this regard, see also [8]).

It is worthwhile to note the following points regarding the last example.

(i) The control system that one would obtain within the realm of classical mechanics is identical to the one in the example above—the sole difference being that q and p represent the conjugate position and momenta, and not their averages. In addition, since the controllability rank condition in the example above does not involve either the q's or the p's, the quantum system, with expectation values of the p's and the q's as its state, is controllable whenever the classical system is.

(ii) The fact that the controllability of a linear control system can be checked via a simple rank criterion which, in addition, does not vary from point to point (in the state space) is an important property which is usually not valid for a nonlinear control system. For analytic nonlinear systems there are analogous rank criteria (which involve Lie brackets) which are coordinate dependent in general and furthermore do not guarantee controllability as we have defined it in this paper, but only ensure a somewhat weaker property (from a practical point of view) called accessibility (see [9]). When one of these criteria is specialized to linear control systems one obtains the well-known Kalman rank criterion. The linearity ensures the coordinate independence and also yields, in its wake, the stronger property of controllability. Invariant systems on compact Lie groups are similar to linear systems in this regard, as we will explain in Sec. III. In some respects, they are even better because if one can show that for such a system it is possible to transfer the state from one point to another then, in fact, the same transfer can be achieved with an external control whose amplitude is bounded by any positive constant of choice. There is yet another point of similarity between linear systems and invariant systems on Lie groups. This has to do with optimal control. For linear control systems the problem of finding a control which not only achieves transfer of state but also minimizes a quadratic cost criterion reduces to solving a matrix Riccati equation. This is not true for a nonlinear control system, where the same problem is decidedly more difficult. On the other hand, the same problem for invariant systems on Lie groups admits a solution simpler than that for an arbitrary smooth nonlinear system. However, the computations for an invariant system are usually harder than those for a linear system (see [10]).

III. CONTROLLABILITY OF INVARIANT SYSTEMS ON LIE GROUPS

We will now present the results of [11] regarding the controllability of invariant systems on Lie groups. We refer the reader to [12] for results on the same topic, and for other applications which lead to similar models. Throughout this section we will assume that we are dealing with an invariant system on a Lie group G, with Lie algebra h.

Consider system (4). We will first clarify the most general class of controls that one is allowed to use. These controls will henceforth be called admissible controls. An admissible control is a choice of $u_i(t)$ in system (4), which when substituted into the right-hand side of (4) causes the resulting ordinary differential equation to lead to an initial value problem which has a unique solution. Thus, for instance, one can take $u_i(t)$ to be any piecewise differentiable function of t, though one can easily get by with less regularity.

Next we will associate with system (4) two Lie algebras of paramount importance.

(i) We first consider the Lie algebra l which is the Lie algebra spanned by the matrices $A, B_1, \ldots, B_m$. This means that l, as a set, consists of all possible (real) linear combinations of $A, B_1, \ldots, B_m$ and all possible iterated Lie brackets of $A, B_1, \ldots, B_m$. Of course, l is a Lie algebra by its very construction. Let us denote the connected Lie group, corresponding to the Lie algebra l, by S.

(ii) The second Lie algebra that we will introduce will be denoted by the symbol l_0. l_0 is the ideal generated by the matrices $B_1, \ldots, B_m$ in the Lie algebra l (see [6,7] for a definition of an ideal). In practice, this means that l_0 contains all possible finite (real) linear combinations of (i) $B_1, \ldots, B_m$; (ii) all possible iterated Lie brackets of the $B_1, \ldots, B_m$ among themselves; and (iii) all possible iterated Lie brackets of all the members of the sets in (i) and (ii) with A. l_0 differs from l in that it need not contain A itself. A will belong to l_0 if, and only if, A can be written as a finite (real) linear combination of any basis of l_0. Once again, by its very construction, l_0 is also a Lie algebra. We denote the connected Lie group corresponding to it by the symbol S_0. S_0 is a subgroup of the group S. Furthermore, l_0 will have a dimension of either one less than that of l or equal to that of l.

Before we state the theorems required for our purposes we will recall the definition of controllability.

Definition 3.1. The control system (4) is said to be controllable if, given any two matrices V and W in G, there exists an admissible control $u_i(t), i=1, \ldots, m$ which will transfer the state of (4) from the matrix V at time $t=0$ to the matrix W at some future, finite time T. We define the reachable set from U at a given, positive, finite time t_{final} to be the set of all matrices which have the property that there exists an admissible control which will transfer the state of (4) from V at time $t=0$ to them at time $t=t_{\text{final}}$. Finally, the reachable set from the matrix V is the union, over all finite, and positive T_{final}'s, of the reachable set from V to t_{final}.

We are now ready to state the following.

Theorem 3.1. The reachable set at time t_{final} from the identity matrix is contained in the coset of S_0 in S which contains the matrix $e^{t_{\text{final}} A}$.

Theorem 3.2. The reachable set from the identity matrix in G is contained in S. If S is compact then the reachable set from the identity matrix equals S. In particular, if the dimension of the Lie algebra l equals the dimension of the ambient Lie group G, and the Lie group G is compact, then the control system (4) is controllable. Furthermore, in this case it is possible to reach any matrix with an admissible control which is bounded in amplitude by an arbitrary finite set of constants [i.e., one can choose $u_i(t)$ to satisfy the inequalities $|u_i(t)| \leq K_i$, for any choice of positive, finite constants $K_i, i=1, \ldots, m$].

The following points are worthy of attention.

(i) The first theorem holds even if the ambient Lie group is not compact. However, even if it is compact one cannot conclude the equality of the reachable set at time t_{final} with the corresponding coset of S_0.

(ii) In the second theorem it is crucial that the G be compact.

(iii) We reiterate that if one can find any control that achieves transfer of state from a given initial condition to a desired final one, then there also exists controls whose amplitude may be constrained by an positive number one chooses, and which achieves the same transfer of state at a possibly later final time.

IV. CONTROLLABILITY OF FINITE-LEVEL QUANTUM SYSTEMS

We can now specialize to the case of a finite-level molecular system. The control system (4) now becomes system (3). One can assume that the A matrix is diagonal, with purely imaginary entries and with nonzero trace. Also, it is typically the case that in these applications there is only one external control, i.e., $m=1$ in (3), since only one external laser field is usually available. The results that we will state below are valid even if there are more controls, and if one does not work in the eigenbasis of the internal Hamiltonian (i.e., if the corresponding A is not diagonal). The only reason we are making these simplifying assumptions is the calculations for the Lie algebras l and l_0 become that much easier. We now have the following results.

Theorem 4.1. All coherent superpositions of states can be achieved if S equals $U(N)$. This is equivalent to requiring that l be the Lie algebra of all $N \times N$ skew-Hermitian matrices, which in turn is equivalent to requiring that the dimension of l as a vector space over the real numbers is precisely N^2. The latter two of the above equivalent conditions are also necessary for controllability.

Proof: This is just a consequence of Theorem 3.2 and the fact that the Lie group $U(N)$, which is the ambient group for the control system (3) is compact and has dimension N^2.

Theorem 4.2. All probability amplitudes can be achieved if S is compact and contains $SU(N)$ which is equivalent to demanding that l is the Lie algebra of all $N \times N$ skew-Hermitian matrices. In particular, if all probability amplitudes can be achieved then one can obtain all coherent superpositions of states.

Proof: This follows by combining the results of Theorem 3.2 and Proposition 2.1. Indeed, if the reachable set from the identity matrix contains or even, just equals $SU(N)$ then Proposition 2.1 immediately guarantees the conclusion. Since, $SU(N)$ and $U(N)$ are both compact, a sufficient condition for this to happen, by virtue of Theorem 3.2 is that l equals or contains $su(N)$. Now, l can never equal $su(N)$ because A does not have zero trace and thus cannot belong to $su(N)$, whereas by definition it belongs to l. Hence a sufficient condition for being able to achieve all probability amplitudes is that l equal $u(N)$. Indeed, in this case since $U(N)$ is compact, Theorem 3.2 assures us that the reachable set from the identity matrix is $U(N)$, which certainly contains $SU(N)$. This condition is also necessary because if l is to contain $su(N)$ but not equal it then it has to necessarily equal $u(N)$. This point follows because the difference in the dimensions of $u(N)$ and $su(N)$ is 1, and this is also the difference in the dimensions of $su(N)$ and l, given that the latter contains $su(N)$.

Remark 4.1. It also follows that, under the hypotheses of the previous theorem, one can achieve all admissible expectation values of any physical observable of interest.

We will now briefly outline an implementable algorithm for ascertaining the controllability of a finite-level quantum system. The first step is to develop the Lie algebra l_0 from the matrix representations of the internal and interaction Hamiltonians. It ought to be clear from the proof of the last theorem that to ascertain controllability one does not need to find l, since the knowledge of l_0 reveals the dimension of l as well. To determine l_0 we proceed as follows. We identify each of the matrices A and B of (3) with a column vector in R^{N^2}, i.e., we choose some ordering of the N^2 independent elements of a skew-Hermitian matrix and consistent with that ordering list these elements in a column. Since these matrices belong to finite-dimensional Lie algebras [$u(N)$ or $su(N)$] the computation of the Lie algebras l and l_0 will, of necessity, terminate in a finite number of steps. The following steps are then carried out to generate l_0.

(1) We divide the aforementioned column vector representation of the matrix B by its norm to obtain a unit vector in that direction. Note that if we had more than one input, we would perform the Gram-Schmidt orthogonalization procedure on the corresponding column vectors in this step.

(2) To the set generated by the orthogonal set of columns in step (1) above, we append the set of all column representations of the Lie brackets of members of the set in step (1) and their Lie brackets with A.

(3) The rank of the set developed in step (2) is evaluated. If it equals the rank of the set from step (1), then all iterations are stopped and the set obtained in step (1) is precisely l_0. If this is not satisfied then step (4) is performed.

(4) Substitute the new set as the initial set in step (1) and perform steps (1) and (2).

Remark 4.2. Suppose the dimension of l is less than N^2 (equivalently if the dimension of L_0 is less than N^2-1). Denote the corresponding connected Lie subgroup of $U(N)$ by H. Suppose that H is a compact subgroup of $U(N)$. Therefore, Theorem 3.2 applies in the situation at hand. In particular, given some initial condition $\mathbf{a}_0$ of system (2) we can identify the set of states that can be obtained from $\mathbf{a}_0$ via an external laser field with the set $\{h\mathbf{a}_0, h \in H\}$. Note that in molecular control problems l differs from l_0 by A. Therefore we do not need a separate algorithm for l. In practice, H may not be easy to determine. However, the fact that consists H precisely of all possible finite products of matrix exponentials of any basis (in particular, the basis obtained by the algorithm of this section) of l may be handy in particular situations.

V. EXAMPLES AND RESULTS

In this section we will analyze an example taken from [5]. This example concerns a particular five-level system. Based on their optical control calculations the authors believed that they could achieve any desired probability amplitude. We establish the validity of their assertions using the results of Sec. IV.

The matrix representations of the internal Hamiltonian and the dipole are given by

$$H_0 = \begin{bmatrix} 1.0 & 0 & 0 & 0 & 0 \\ 0 & 1.2 & 0 & 0 & 0 \\ 0 & 0 & 1.3 & 0 & 0 \\ 0 & 0 & 0 & 2.0 & 0 \\ 0 & 0 & 0 & 0 & 2.15 \end{bmatrix}$$

and

$$H_1 = \begin{bmatrix} 0 & 0 & 0 & 1 & 1 \\ 0 & 0 & 0 & 1 & 1 \\ 0 & 0 & 0 & 1 & 1 \\ 1 & 1 & 1 & 0 & 0 \\ 1 & 1 & 1 & 0 & 0 \end{bmatrix} .$$

The Lie algebra l_0, corresponding to this choice of the matrix representations of the internal and external Hamiltonians, was generated using the algorithm of Sec. IV, and was found to be equal to su(5). One cannot immediately conclude that all coherent superpositions can be obtained, even if we interested in achieving the same only up to arbitrary phase. We still have to evaluate the Lie algebra l. But this Lie algebra equals u(5). To arrive at this conclusion we perform a dimension count. The dimension of l_0 equals that of the Lie algebra su(5) which is 24. Now the dimension of l, which differs from l_0 in that it contains the matrix H_0, has to be 25 because H_0 has nonvanishing trace and thus cannot belong to su(5). Consequently it contributed one extra dimension. Hence, one can conclude that the Lie algebra l equals u(5), as it was known to be contained in u(5) and has dimension equal to that of u(5) (namely 25). One can now conclude that all coherent superpositions can be obtained in some finite terminal time T.

We remark that in low-dimensional cases the reader can verify controllability by hand computations. To simplify these computations a basic observation needs to be made, viz that, in order to conclude controllability (up to an arbitrary phase), it is adequate to come up with N^2-1 linearly independent (over the real numbers) skew-Hermitian matrices (arising from the internal and external Hamiltonians of the problem under consideration). To facilitate this process we take advantage of the fact that in typical multiple-level system examples, both H_0 and H_1 have all entries real. Thus matrices A and B have purely imaginary entries. In particular, this means that their Lie bracket $[A,B]$ is a matrix which has all entries real, and thus is automatically guaranteed to be linearly independent from B as long as it is not identically zero. At the next step, the matrix $[A,[A,B]]$ is purely imaginary and is thus linearly independent from $[A,B]$, though not necessarily from B (as long as $[A,[A,B]]\neq 0$). Of course, one may just as well consider $[B,[A,B]]$. All that one needs to do is to generate N^2-1 linearly independent skew-Hermitian matrices, and if N is small the process will terminate soon for the reasons outlined above.

VI. CONCLUDING REMARKS AND OBSERVATIONS

We have introduced issues related to the notion of controllability, especially in the context of quantum molecular dynamics. We have used finite-dimensional models as the starting point for our investigation. For a variety of practical reasons one necessarily has to work with finite-level models. However, certain results obtained in such a manner may well be only an artifact of the truncation. To illustrate what we mean, consider a three-level system. Suppose that, initially, only the ground level is populated. Suppose, furthermore, that in this model populating the third level corresponds to breaking the stronger of two bonds in a triatomic molecule and populating the second level implies breaking the weaker of the two bonds. Now, imagine that by analyzing the Lie algebra L one arrives at the conclusion that the control system describing the evolution of the unitary generator of this finite-level quantum system is controllable, and therefore so is the finite-level system. However, one must proceed with care in concluding that the stronger of the two bonds can be broken in the laboratory. This point arises because all that the controllability at the level of unitary generators means is that starting from the identity matrix one will be able to produce one of the unitary matrices which transforms the vector $(e^{i\theta},0,0)^t$ to the vector $(0,0,e^{i\alpha})^t$ in some finite time interval. What the result does not guarantee is that the trajectories of the system, under such an external field, will not run through those unitary matrices which cause the second level to be nearly populated before it arrives at the unitary matrix which causes the third level to be populated. Hence due caution is needed. It is still very important, however, to establish whether a molecular system is controllable. Knowledge of its controllability is important if one is not to go after futile goals. On the other hand, armed with the knowledge of its controllability, one can attempt to seek an external field which will produce the desired unitary generator as the solution to an optimal control problem with penalties on straying too close to the unitary generators which will cause undesired states to be produced. Alternatively, one could pose an optimal control problem at the level of the probabilities themselves, with penalties on the frequencies of the external field. There is reason to be optimistic that a controllability analysis will have ample *practical* significance. In [13] Schrödinger's equation (with an external time-varying field) was linearized with respect to the external field and then truncated to a finite number of modes to obtain a finite-dimensional linear control system. The Kalman rank criterion, discussed in this paper, was applied to this system to check its controllability. Under some very natural stipulations this control system was shown to be controllable. Since the system is linear one can compute explicitly, from first principles alone, the external field which will cause the state of the system to be transferred to a desired final state (a similar result is not available for an arbitrary nonlinear system). The external field derived in [13] was such that only the correct excitation frequencies were excited (i.e., those inducing resonant transitions), thereby avoiding the problem alluded to above. Similarly, in [14] a field, which was both bounded in amplitude and had only the correct excitation frequencies, was developed for selective population of multilevel systems. This was generated by a "feedback" law.

Finally we will compare our techniques with those of a paper with similar intent [3]. In [3], the authors study the controllability of Schrödinger's equation by construing it as an infinite-dimensional bilinear system. By exploiting the analogy between Lie brackets of vector fields (on an infinite-dimensional manifold) and the Heisenberg bracket of the corresponding operators, they sought to establish algebraic criteria for the controllability of the system under study. However, as they point out, the infinite dimensionality of the ambient manifold precludes any chance of finitely computable criteria being able to conclude controllability. Consequently, they address the problem of controllability of states belonging to a finite-dimensional submanifold. However, this submanifold need not *a priori* represent states of physical interest. There are, in our opinion, two drawbacks to the aforementioned approach. Both have to do with the fact that the algebraic criteria for an arbitrary nonlinear system (even bilinear system) are not adequate to yield conclusions about controllability (as we have defined it, and as is desirable from a physical point of view). The algebraic rank criteria, when satisfied, yield only the weaker property of accessibility. This is much weaker than asserting that every state can be obtained. Furthermore, there is no result available for an arbitrary bilinear system which guarantees controllability with external fields which are weak in amplitude. On the other hand, neither of the above restrictions occurs for invariant systems on compact Lie groups. This is, in fact, the primary reason for our preference for an analysis of the controllability of the equation for the evolution of the corresponding unitary generators. The price we have to pay for this is the attendant Galerkin approximation. However, there is adequate reason to be optimistic that the neglected modes will not affect the controllability in any serious manner (see [14]). The passage to the unitary generators enables us to derive a verifiable set of criteria, in a self-contained manner, without resort to any complicated mathematical analysis.

We would like to conclude by suggesting some directions for further research.

(i) Study a broad family of physically interesting finite-level quantum control problems at the level of the corresponding unitary generators. There is a general philosophy to the effect that invariant systems on Lie groups enjoy properties, of a level of simplicity and utility, comparable to those of linear control systems. Of course, as with all philosophies, there are exceptions (see [15]).

(ii) The controllability algorithm described here does not depend on the particular representation chosen for the Hamiltonian. However, expressing them in spherical tensor operators, or other symmetry-adapted operators may be especially useful. In many cases the problem of ascertaining controllability will reduce to a sequence of tests on sub blocks of the Hamiltonian matrix.

(iii) Different types of controllability definitions should be formulated that appropriately capture the molecular control problem. We suggest two which are closely related to the types of problems considered here, but others also exist. One can consider Schrödinger's equation, with an interaction Hamiltonian, as an infinite-dimensional bilinear control system, and then examine conditions under which any specified number of finite modes can be controlled. Clearly this is the best one can hope for, in general. A second issue is related to the characteristics of the control law which achieves the transfer of states given that the underlying finite-level quantum system is indeed controllable. As mentioned already, one of the main virtues of passing to an analysis of an invariant system on a compact Lie group [U(N), in our case] is that if one could show that a particular terminal state could be attained, with external fields which are not restricted in amplitude, then it can be shown that the same state may be attained with an external field with bounds on its amplitude. However, there are no similar results available for the frequency spectrum of the external laser field. The results of [14] resolve this problem for problems where the goal is the selective excitation of states. We have made some progress on the general case via methods which make use of the Lie algebraic structure of the algebra l associated with (2). The obvious remedy, for the general case of a coherent superposition of states, would seem to be to study the controllability of the system with amplitude and frequency restrictions. However, the control system obtained in this fashion is nonlinear but time varying. This makes the analysis rather difficult.

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