126, 457 (1994); D. G. Pearson *et al*., *ibid*. **134**, 341 (1995); D. G. Pearson *et al*., *Geochim. Cosmochim. Acta* **59**, 959 (1995).
28. S. B. Shirey, J. F. Bender, C. H. Langmuir, *Nature* **325**, 217 (1987); C. J. Hawkesworth, M. S. M. Mantovani, P. N. Taylor, Z. Palacz, *ibid*. **322**, 356 (1986); J. Mahoney, A. P. LeRoex, Z. Peng, R. L. Fisher, J. H. Natland, *J. Geophys. Res.* **97**, 19 (1992); J. J. Mahoney, W. M. White, B. G. J. Upton, C. R. Neal, R. A. Scrutton, *Geology* **24**, 615 (1996).
29. R. S. White, *Nature* **327**, 191 (1987); _____ and D. McKenzie, *J. Geophys. Res.* **94**, 7685 (1989).
30. F. A. Frey *et al*., *Earth Planet. Sci. Lett.* **144**, 163 (1996).
31. R. D. Müller, J.-Y. Royer, L. A. Lawver, *Geology* **21**, 275 (1993); B. C. Storey, *Nature* **377**, 301 (1995).
32. R. A. Duncan, *J. Volcan. Geotherm. Res.* **4**, 283 (1978).
33. The variation of $^{187}Os/^{188}Os$ and Os concentration do not appear to correlate with any petrographic features or incompatible trace-element abundances.
34. Our samples were collected during the 1992 to 1993 austral field season. We thank A. Giret, F. Frey, D. Weis, and J.-Y. Cotin for assistance in sampling. We also thank G. Ravizza for discussions, S. Hart for sharing of laboratory facilities, J. Blusztajn for advice, K. Burrhus for technical support, E. Nakamura for Sr isotopic analysis of OB93-78 cpx, and F. Frey and M. F. Roden for comments. N.S. acknowledges support from the National Geographic Society (4629-91) and the National Science Foundation (EAR-9219158 and OPP-9417806). This research is also supported by a Cecil and Ida Green Fellowship to D.R.H.

21 January 1998; accepted 26 February 1998

Unitary Control in Quantum Ensembles: Maximizing Signal Intensity in Coherent Spectroscopy

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Experiments in coherent magnetic resonance, microwave, and optical spectroscopy control quantum-mechanical ensembles by guiding them from initial states toward target states by unitary transformation. Often, the coherences detected as signals are represented by a non-Hermitian operator. Hence, spectroscopic experiments, such as those used in nuclear magnetic resonance, correspond to unitary transformations between operators that in general are not Hermitian. A gradient-based systematic procedure for optimizing these transformations is described that finds the largest projection of a transformed initial operator onto the target operator and, thus, the maximum spectroscopic signal. This method can also be used in applied mathematics and control theory.

The development of specific sets of controlling unitary transformations (pulse sequences) has long been a major thrust in nuclear magnetic resonance (NMR) spectroscopy (*1*) and, more recently, in electron magnetic resonance spectroscopy (*2*), laser coherent control (*3*), and quantum computing (*4*). These spectroscopic experiments are most often applied to quantum ensembles rather than individual atoms or molecules. For example, a test tube of water may contain some 10^{22} hydrogen atoms, and a full quantum-mechanical description would afford $2^{10^{22}}$ spin energy levels; yet, a reduced density operator treatment (*5*, *6*) with no more than four highly averaged matrix elements gives an excellent description of its spin dynamics.

In sufficiently large quantum ensembles, the expectation values of noncommuting operators, such as I_x and I_y, can be determined simultaneously with negligible mutual interference. For example, in NMR it has been customary to record the magnetization from an ensemble along the *x* and *y* axes simultaneously in the rotating frame. The complex superposition of the two signals is called quadrature detection and corresponds to the non-Hermitian detection operator $I^+ = I_x + iI_y$ (*1*) (where $i = \sqrt{-1}$). Moreover, non-Hermitian components of the density operator, such as I^+, can be distinguished experimentally from their adjoints (in this case from I^-) by their different responses to rotations around the quantization axis *z*. This makes them amenable to filtering by pulsed field gradients and coherence transfer echoes and also results in opposite signs of their oscillation frequencies during evolution or detection periods. Consider, for example, a standard two-dimensional (2D) NMR experiment with an evolution period t_1 and a detection period t_2. In order to maximize the intensity of 2D peaks, two successive transformations must be optimized. In a first step, the density operator containing the operators I_z that represent the ensemble of nuclear spins at thermal equilibrium is transformed into a state including non-Hermitian operators like I^+ or products of such operators oscillating during t_1. In a second step, these non-Hermitian operators must be transformed to yield non-Hermitian operators I^- that are detected by I^+ during t_2. Almost all multidimensional NMR experiments require optimal transfers between operators that are in general not Hermitian. A procedure to find unitary transformations of a given operator *A* achieving the largest projection onto a target operator C (where both may take the form of an arbitrary complex square matrix) is highly desired not only by the experimentalist; in this general case, it has so far also been an unsolved problem to the mathematicians (*7*).

In this context, we address the following questions. (i) What are the unitary transformations of a given initial operator *A* that maximize the transfer amplitude onto a target operator C, and what is the maximum amplitude? (ii) What additional restrictions are imposed by symmetry or a limited set of experimentally available control fields?

For the transformation between an initial quantum-mechanical state function $|\psi_i\rangle$ and a target state function $|\psi_t\rangle$ of the same norm, it is always possible to find a unitary operator *U* that converts $|\psi_i\rangle$ completely into $|\psi_t\rangle$, that is, $U|\psi_i\rangle = b|\psi_t\rangle$ with $b = 1$. In this case, the transfer amplitude is only restricted by experimental constraints (*8*). This argument also holds for an ensemble in a pure state where all individual quantum systems can be described by the same state function $|\psi\rangle$. However, the situation is quite different for nonpure states. Suppose the operator *A* represents a (not necessarily Hermitian) component of the density operator (*5*, *6*) relevant to a specific signal in a spectroscopic experiment. If relaxation and other dissipative processes can be neglected, *A* is transformed during the experiment by a unitary transformation of the form

$$\tilde{A} = UAU^\dagger \qquad (1)$$

where the propagator *U* is a unitary operator (*9*). In contrast to unitary transformations between two normalized state functions $|\psi_i\rangle$ and $|\psi_t\rangle$, it is in general not possible to transform an arbitrary initial

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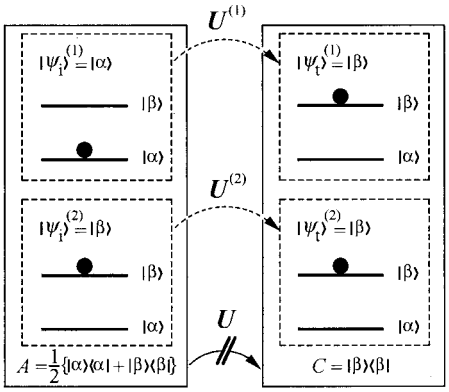

Fig. 1. Individual unitary transformations $U^{(1)}$ and $U^{(2)}$ exist, taking the initial state functions $|\psi_i\rangle^{(1)} = |\alpha\rangle$ and $|\psi_i\rangle^{(2)} = |\beta\rangle$ to the target state functions $|\psi_t\rangle^{(1)} = |\beta\rangle$ and $|\psi_t\rangle^{(2)} = |\beta\rangle$, respectively. However, for the ensemble consisting of both quantum systems, there is no unitary transformation U that transforms the initial density operator $A = \frac{1}{2}\{|\alpha\rangle\langle\alpha| + |\beta\rangle\langle\beta|\}$ completely into the target density operator $C = |\beta\rangle\langle\beta|$. In general, if $A_\varepsilon = \frac{1}{2}\{(1+\varepsilon)|\alpha\rangle\langle\alpha| + (1-\varepsilon)|\beta\rangle\langle\beta|\}$, then $UA_\varepsilon U^\dagger \neq C$ for all U unless $\varepsilon = \pm 1$.

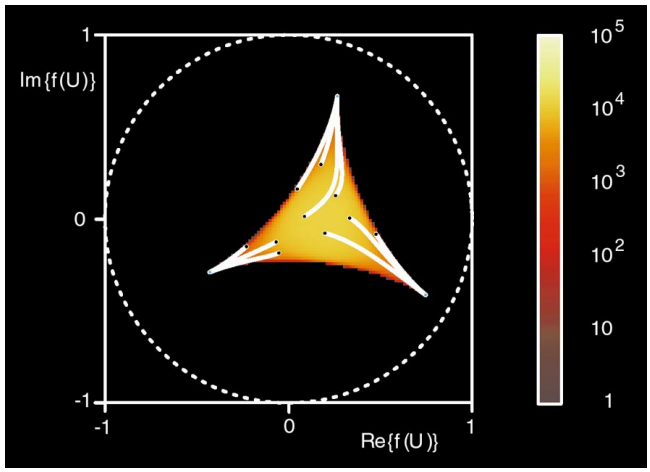

Fig. 2. For two given 3 × 3 matrices A and C (*15*), an image of the C-numerical range $W_C(A^\dagger)$ is generated by calculating $f(U_k)$ for 10^7 random unitary operators U_k. The range between ±1 (Re axis) and $\pm i$ (Im axis) of the complex plane was partitioned into 128 by 128 pixels, and the number of hits per pixel is color coded. In addition, for 10 arbitrarily chosen initial unitary operators U_0, the values of $f(U_0)$ are indicated (black dots) and the trajectories of $f(U_k)$ are shown during the optimization of $|f(U)|$ (white lines). The dashed white circle corresponds to the norm limit of $|f(U)|$.

operator A completely into any target operator C (Fig. 1). Hence, a fundamental limit of quantum control is imposed by the properties of unitary transformations of operators. The task is to maximize the overlap between the transformed operator $\tilde{A}$ and the target operator C, the extent of which can be quantified by the scalar product $\langle\tilde{A}|C\rangle$ (*9*). In mathematics, the set of all possible values of $\langle\tilde{A}|C\rangle$ for arbitrary unitary operators U is called the C-numerical range of $A^\dagger$, denoted $W_C(A^\dagger)$ (*7*, *10*). The maximum attainable absolute value of $\langle\tilde{A}|C\rangle$ constitutes a fundamental unitary bound b for the achievable transfer amplitude between A and C. In the mathematical literature, this bound is called the C-numerical radius of $A^\dagger$, written $r_C(A^\dagger)$ (*10*). Whereas the problem of determining the least upper bound has been solved for transfers between Hermitian operators (*11*), the one between non-Hermitian operators is so far unsolved (*7*).

Here we introduce a method to determine the fundamental bound b equivalent to $r_C(A^\dagger)$ for arbitrary complex operators A and C. In addition, the method yields unitary operators U_{opt} achieving it. We restrict the following discussion to Liouville spaces of finite dimension where all operators can be represented by complex square matrices. For simplicity and without loss of generality, we assume that A and C are normalized to a trace norm of 1 (*9*). Then the function

$$f(U) := \langle UAU^\dagger|C\rangle \qquad (2)$$

maps any unitary operator U onto a complex number, and the unitary bound b corresponds to the maximum of the real-valued function $|f(U)|$

$$b = \max_U |f(U)| \qquad (3)$$

An iterative algorithm to identify b can be constructed if for any U in the space of unitary operators the gradient $\nabla|f(U)|$ is known or, more conveniently, the gradient $\nabla F(U)$ for the function $F(U) = |f(U)|^2$. It takes the form (*12*)

$$\nabla F(U) = \{(f^*(U)[UA^\dagger U^\dagger, C])^\dagger - f^*(U)[UA^\dagger U^\dagger, C]\}U \qquad (4)$$

If, for a given unitary operator U_k, the gradient $\nabla F(U_k)$ does not vanish, the following iterative scheme finds a unitary operator U_{k+1} with $|f(U_{k+1})|$ closer to the unitary bound b (*12*)

$$U_{k+1} = \exp\{-\delta\nabla F(U_k)U_k^\dagger\}U_k \qquad (5)$$

where $\delta > 0$ is an adaptable step size (*13*). This algorithm is an Euler-type approach modified to ensure that the operators U_{k+1} remain unitary. It generalizes methods optimizing transfer between real symmetric matrices (*14*) to the general case of complex square matrices.

This algorithm is illustrated in Fig. 2 for an example of low dimensionality (*15*), where an approximation to the corresponding C-numerical range $W_C(A^\dagger)$ is readily obtained by calculating $f(U)$ for a large number of random unitary operators U that are created by orthonormalizing the columns of a random complex matrix using a Gram-Schmidt procedure. However, this approach is impractical as soon as the problem is of higher dimension. Figure 2 also shows typical trajectories (compare with Eq. 5) of $f(U_k)$ during the optimization of 10 arbitrary initial unitary operators U_0. Even in the presence of several local maxima, the desired global maximum b of $f(U)$ can be determined by tracing the boundary of the C-numerical range (*12*) (Fig. 3).

For non-Hermitian operators of interest in spectroscopic applications (*16*), all local maxima of $|f(U)|$ are equivalent because the corresponding C-numerical ranges are circular disks centered at the origin of the complex plane (*17*–*19*). In these cases, the unitary bound b and an optimal unitary operator U_{opt} are found using the simple gradient-based optimization starting from a single initial unitary operator U_0. For example, consider non-Hermitian operators A and C representing an ensemble of I_nS spin systems. Each I_nS spin system consists of n spins-$\frac{1}{2}$, denoted I_1, . . . , I_n (for example ^{1}H nuclear spins) and one additional spin-$\frac{1}{2}$, denoted S (such as a ^{13}C nuclear spin or an electron spin). A transformation of practical interest (*20*) is the transfer of −1 quantum coherence of spin S to −1 quantum coherence of the I spins with the initial operator $A = S^- = S_x - iS_y$ and the target operator $C = F^- = \sum_{k=1}^n (I_{kx} - iI_{ky})$ (*9*, *21*). The unitary

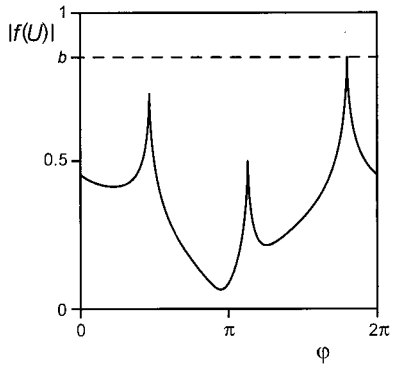

Fig. 3. For the case of Fig. 2, the absolute value $|f(U)|$ is shown as a function of φ for all points on the boundary of the C-numerical range $W_C(A^\dagger)$ (*12*). The global maximum of $|f(U)|$ yields the unitary bound $b = 0.85$.

Table 1. Maximum transfer efficiencies for typical coherence transfer processes in I_nS (n = 1, 2, and 3) spin systems. Singular value conservation yields $u^{(SV)}$ (*23, 24*), which forms an upper limit to the fundamental unitary bound b. In cases with permutation symmetry among the n I spins, $u'^{(SV)}_{sym}$ (*28*) forms an upper limit of the attainable unitary bound b'_{sym}, and exp_{sym} corresponds to the best transfer efficiencies provided by state-of-the-art experiments (*20*).

Transfer	Spin system	$u^{(SV)}$	$u'^{(SV)}_{sym}$	b	b'_{sym}	exp_{sym}
$S^- \rightarrow F^-$	IS	1	1	1	1	1
	I_2S	1	$\frac{3}{4} = 0.75$	$\frac{1}{\sqrt{2}} = 0.707$	$\frac{3\sqrt{3}}{8} = 0.650$	$\frac{4\sqrt{2}}{9} = 0.629$
	I_3S	$\frac{2+\sqrt{3}}{4} = 0.933$	$\frac{3+4\sqrt{3}}{12} = 0.827$	$\frac{3+\sqrt{3}}{6} = 0.789$	$\frac{3+\sqrt{3}}{6} = 0.789$	$\frac{1}{\sqrt{3}} = 0.577$
$2F_zS^- \rightarrow F^-$	IS	1	1	1	1	1
	I_2S	$\frac{1}{\sqrt{2}} = 0.707$	$\frac{1}{\sqrt{2}} = 0.707$	$\frac{1}{\sqrt{2}} = 0.707$	$\frac{1}{\sqrt{2}} = 0.707$	$\frac{1}{\sqrt{2}} = 0.707$
	I_3S	$\frac{7+2\sqrt{3}}{12} = 0.872$	$\frac{8+\sqrt{3}}{12} = 0.811$	$\frac{1+2\sqrt{3}}{6} = 0.744$	$\frac{1+2\sqrt{3}}{6} = 0.744$	$\frac{5}{8} = 0.625$

bounds b determined for these transfers with the gradient-based algorithm are given in Table 1. For the I_2S spin system, typical trajectories of $f(U)$ during the optimization of $|f(U)|$ are shown in Fig. 4. As expected (*18, 19*), all trajectories converge to the same value $|f(U_{opt})| = 1/\sqrt{2} = 0.707$, which represents the previously unknown unitary bound b for this transfer. Figure 4 also shows that the density of $f(U)$ for randomly chosen U decreases rapidly with increasing $|f(U)|$. Even when $f(U)$ was evaluated for 10^7 randomly chosen unitary operators U, the largest value of $|f(U)|$ found was <66% of the unitary bound b, as even 10^7 trials sample only a small portion of the high-dimensional space (*22*).

It is interesting to compare the fundamental unitary bound with known upper and lower limits for b (*7, 10*)

$$0 \leq l^{(EV)} \leq b \leq u^{(SV)} \leq 1 \qquad (6)$$

Because the norm of an operator is invariant under unitary transformations (*9*), the unitary bound b cannot exceed 1. This upper limit for b can be further tightened to $u^{(SV)}$ by noting that unitary transformations also conserve the singular values of an operator (*23, 24*). A lower limit $l^{(EV)}$ for b results from conservation of eigenvalues of an operator under unitary transformations (*25*). Only for the special case of Hermitian operators A and C, where $b = l^{(EV)}$ (*11, 26*), are exact bounds known so far. However, in the general case of non-Hermitian operators A and C, b is only poorly defined by these upper and lower limits. For example, for the transfer between $A = S^-$ and $C = F^-$ in I_nS spin systems, all eigenvalues of A and C are 0, and hence, the lower limit $l^{(EV)} = 0$ is useless. The corresponding upper limits $u^{(SV)}$ are also summarized in Table 1.

So far, the discussion has been restricted to the determination of the fundamental unitary bound b defined in Eq. 3. However, this bound is only relevant in practice if arbitrary unitary transformations can be implemented experimentally (*27*). Moreover, the new approach is also suited to determine upper bounds for transfer efficiencies if only a subset U' of all unitary operators U is available. Then $|f(U'_{opt})|$ corresponds to the reachable bound $b' \leq b$. This condition holds if, for example, the system investigated shows permutation symmetry. These restrictions can be taken into account in a symmetry-adapted basis with the matrix representations of the operators A and C assuming block structure (*1, 28*). For each block j, an optimal unitary suboperator and a unitary bound b'_j can be derived separately. Then the final unitary operator is the direct sum of the unitary suboperators and $b'_{sym} = \Sigma_j b'_j$.

Table 1 summarizes the symmetry-restricted unitary bounds b'_{sym} and their upper limits $u'^{(SV)}_{sym}$ (*28*) for the transfer between $A = S^-$ and $C = F^-$ in I_nS systems with equivalent spins $I_1, \ldots, I_n$. For I_2S systems, the best known experimental implementation (*20, 29*) almost achieves the unitary bound b'_{sym}. However, in I_3S spin systems, <75% of the unitary bound $b = b'_{sym}$ has been reached so far, thus leaving considerable room for improvement. A similar situation exists for the transfer between the operators $A = 2F_zS^-$ and $C = F^-$ in I_nS systems (*16, 20, 21*) (see Table 1), suggesting that many important experimental building blocks will turn out to be less than optimal, thus triggering a search for better experiments.

In practice, the optimal unitary operator $U = U_{opt}$ typically has to be realized by propagators (*27*) in terms of a finite set $\mathcal{H}$ of effective (that is, time independent) Hamiltonians according to

$$U = \exp(-it_kH_k) \cdot \exp(-it_{k-1}H_{k-1}) \cdot \ldots \cdot \exp(-it_1H_1) \qquad (7)$$

where $t_j > 0$ and $H_j \in \mathcal{H}$ are chosen to

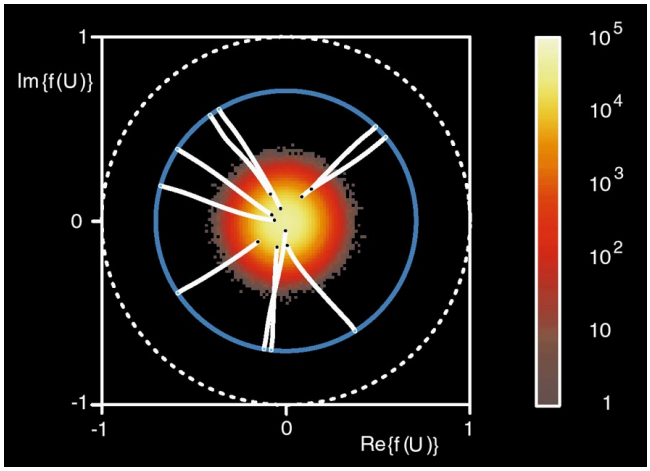

Fig. 4. For the operators $A = S^-$ and $C = F^-$ in an I_2S spin system, the values of $f(U_k)$ are shown for 10^7 random unitary operators U_k. Partitioning and color coding is the same as in Fig. 2. Again for 10 arbitrarily chosen initial unitary operators U_0, the trajectories of $f(U_k)$ during the optimization of $|f(U)|$ are shown as white lines and the radius of the dashed white circle corresponds to the norm limit. The blue circle circumscribes the C-numerical range $W_C(A^\dagger)$, which is a circular disk with radius $b = 1/\sqrt{2}$.

provide the maximum transfer efficiency. Furthermore, the shortest overall duration $\tau = t_1 + t_2 + \ldots + t_k$ is highly desired. This leads to the minimal-time problem min τ subject to

$$U(\tau) = U_{opt}, \qquad \frac{dU(t)}{dt} = -iH(t)U(t) \quad (8)$$

with piecewise constant $H(t) = H_j$ for $\sum_{i=1}^{j-1} t_i \leq t < \sum_{i=1}^{j} t_i$, which is a standard task in optimal control (*30*). Its solution will clearly benefit from the knowledge of the optimum unitary operator and the maximum possible transfer efficiency.

Apart from the spectroscopic impact of controlling quantum ensembles outlined thus far, the approach taken here is readily applicable on a broader scale. It solves the closely related general problem of a least-squares approximation of an arbitrary complex matrix given by the unitary transform of another, as

$$\min \|UAU^\dagger - C\|^2 = \|A\|^2 + \|C\|^2 - 2 \max \mathrm{Re}\ \mathrm{tr}\{UA^\dagger U^\dagger C\} \quad (9)$$

(the function Re takes the real part of the argument). Problems of this kind arise in fitting tasks. Moreover, generalizing the case of real symmetric matrices (*14*), the algorithm is adaptable to sorted diagonalization of complex Hermitian matrices, because the differential equation

$$\frac{dU(t)}{dt} = AU(t)C - U(t)CU^\dagger(t)AU(t) \quad (10)$$

with $U(t)$ unitary induces what is called a gradient flow to the transfer function $\mathrm{tr}\{U^\dagger AUC\}$ by virtue of the trace norm. Thus, if C is some diagonal matrix with sorted real entries, $U(t)$ will finally diagonalize any Hermitian matrix A [by $U^\dagger(t)AU(t)$] to the same ordering of its real eigenvalues as given in C, thus solving a common problem in optimal control.

REFERENCES AND NOTES

1. R. R. Ernst, G. Bodenhausen, A. Wokaun, *Principles of Nuclear Magnetic Resonance in One and Two Dimensions* (Oxford Univ. Press, Oxford, 1987).
2. C. Gemperle and A. Schweiger, *Chem. Rev.* **91**, 481 (1991); A. Schweiger, in *Modern Pulsed and Continuous Wave Electron Spin Resonance*, M. K. Bowman, Ed. (Wiley, London, 1990), pp. 43–118.
3. W. S. Warren, H. Rabitz, M. Dahleh, *Science* **259**, 1581 (1993); H. Rabitz, *Nature* **366**, 304 (1993).
4. G. Taubes, *Science* **275**, 307 (1997); N. A. Gershenfeld and I. L. Chuang, *ibid.*, p. 350; D. G. Cory, A. Fahmy, T. Havel, *Proc. Natl. Acad. Sci. U.S.A.* **94**, 1634 (1997). See also the recent discussion by W. S. Warren [*Science* **277**, 1688 (1997)] and N. Gershenfeld and I. Chuang (*ibid.*, p. 1689). The importance of unitary transformations in quantum ensemble computing was pointed out by D. DiVincenzo [*Phys. Rev. A* **51**, 1015 (1995)].
5. U. Fano, *Rev. Mod. Phys.* **29**, 74 (1957).
6. L. D. Landau, *Z. Phys.* **45**, 430 (1927); J. von Neumann, *Nachr. Ges. Wiss. Göttingen Math. Phys. Kl.* **1927**, 245 (1928); A. Messiah, *Quantum Mechanics* (North-Holland, Amsterdam, 1961); M. Quack, *J. Chem. Phys.* **69**, 1282 (1978); K. Blum, *Density Matrix Theory and Applications* (Plenum, New York, 1981).
7. C. K. Li, T. Y. Tam, N. K. Tsing, *Lin. Multilin. Alg.* **16**, 215 (1984); C. K. Li, *ibid.* **37**, 51 (1994).
8. R. S. Judson, K. K. Lehmann, H. Rabitz, W. S. Warren, *J. Mol. Struct.* **223**, 425 (1990); D. J. Tannor, V. Kazakov, V. Orlov, *NATO ASI Ser. B* **299**, 347 (1992); V. Ramakrishna, M. V. Salapaka, M. Dahleh, H. Rabitz, A. Peirce, *Phys. Rev. A* **51**, 960 (1995).
9. An operator U is unitary if $UU^\dagger = U^\dagger U = Id$, where $U^\dagger$ is the adjoint of U and Id is the identity operator. The scalar product between two operators A and B is given by $\langle A|B\rangle := \mathrm{tr}\{A^\dagger B\}$. The norm (trace norm or Frobenius norm) of an operator A is defined as $\|A\| := \langle A|A\rangle^{1/2}$. For arbitrary operators A and C we define the complex function $f(U)$ as
$$f(U) := \frac{\langle UAU^\dagger|C\rangle}{\|A\|\,\|C\|} = \langle UA_nU^\dagger|C_n\rangle \quad (11)$$
with the normalized operators $A_n = A/\|A\|$ and $C_n = C/\|C\|$. With this definition, $|f(U)|$ is expressed in units of the so-called norm bound (see Eq. 6).
10. A. Horn and C. R. Johnson, *Topics in Matrix Analysis* (Cambridge Univ. Press, Cambridge, 1991); M. Goldberg and E. G. Straus, *Lin. Alg. Appl.* **18**, 1 (1977).
11. O. W. Sørensen, *Prog. NMR Spectrosc.* **21**, 503 (1989); *J. Magn. Reson.* **86**, 435 (1990).
12. See the supplementary material at www.sciencemag.org/feature/data/975625.shl, which contains a formal derivation of the gradient of $|f(U)|^2$ (see Eq. 4) and an algorithm to trace the boundary of $W_C(A^\dagger)$. In all cases investigated and tested, the iterative scheme of Eq. 5 converged at a point on the boundary of $W_C(A^\dagger)$, where the gradient vanishes. At present, a formal proof for this fact exists only for special cases, but we conjecture that local maxima of $|f(U)|$ are always located on the boundary of $W_C(A^\dagger)$.
13. Starting from an arbitrary unitary operator U_0, $|f(U)|$ is optimized using Eq. 5 with a finite step size δ, which in our simple implementation is halved in the course of the optimization whenever $|f(U_{k+1})| < |f(U_k)|$. In practice, the iterative procedure converged more rapidly if in Eq. 5 $\nabla F(U_k)$ was replaced by the normalized operator $\nabla F(U_k)/\|\nabla F(U_k)\|$.
14. R. W. Brockett, in *Proceedings of the IEEE Conference on Decision and Control*, Austin, TX (IEEE, New York, 1988), pp. 799–803); R. W. Brockett, *Proc. Symp. Pure Math.* **54**, 96 (1993); U. Helmke and J. B. Moore, *Optimization and Dynamical Systems* (Springer, Berlin, 1994). As restricted to the real domain, some of the derivatives used in these studies can also be found in H. Lütkepohl, *Handbook of Matrices* (Wiley, New York, 1996).
15. In this example, A and C are the normalized versions of $(e^{i\pi/5}M + Id)$ and $(M + 0.3Id)$, respectively, where M is a diagonal 3×3 matrix with the elements $M_{11} = 1$, $M_{22} = e^{i2\pi/3}$, and $M_{33} = e^{-i2\pi/3}$, and Id is the 3×3 unit matrix. This is a simple example where the C-numerical range $W_C(A^\dagger)$ is neither convex (*7*) nor centered at the origin of the complex plane, which is in contrast to cases of spectroscopic interest (compare with Fig. 4). As the operators A and C are represented by 3×3 matrices, the corresponding space of unitary operators U is nine-dimensional.
16. J. Cavanagh, A. G. Palmer III, P. E. Wright, M. Rance, *J. Magn. Reson.* **91**, 429 (1991); A. G. Palmer III, J. Cavanagh, P. E. Wright, M. Rance, *ibid.* **93**, 151 (1991); L. E. Kay, *J. Am. Chem. Soc.* **115**, 2055 (1993); J. Schleucher *et al.*, *J. Biomol. NMR* **4**, 301 (1994).
17. W.-S. Cheung and N.-K. Tsing, *Lin. Multilin. Alg.* **41**, 245 (1996).
18. In spectroscopic applications, by far the most important class of non-Hermitian density operator components have a defined quantum order $p \neq 0$ (*1*) or are unitarily equivalent to such operators. [An operator A has quantum order p with respect to a quantization axis z if a rotation about z by an angle φ leaves A invariant except for a multiplication with the phase factor $\exp(ip\varphi)$.] In this case, the C-numerical range $W_C(A^\dagger)$ forms a circular disk with radius b centered at the origin of the complex plane (*19*).
19. C. K. Li and N. K. Tsing, *Proc. Am. Math. Soc.* **111**, 19 (1991).
20. M. Sattler *et al.*, *J. Magn. Reson. B* **108**, 235 (1995).
21. In contrast to the definition of $f(U)$ in (*9*) and in Eq. 2, the transfer amplitude as commonly defined in the NMR literature (*11, 24, 28*) is given by
$$a(U) = \frac{\langle UAU^\dagger|C\rangle}{\|C\|^2} = \frac{\|A\|}{\|C\|} f(U) \quad (12)$$
For the I_nS transfers discussed, the norms are $\|S^-\| = \sqrt{2^n}$ and $\|F^-\| = \|2F_zS^-\| = \sqrt{n2^n}$.
22. For an I_2S system, the operators A and C are represented by 8×8 matrices and the corresponding space of unitary operators U is 64-dimensional. For $A = S^-$ and $C = F^-$ in the I_2S case, about 30 iterations are sufficient to determine b with an accuracy of 10^{-6} (initial step size $\delta = 0.2$). This takes about 2 s of CPU time on a μ-VAX 3800. For comparison, the calculation of $f(U_k)$ for 10^7 random unitary operators requires about 48 hours.
23. J. von Neumann, *Tomsk Univ. Rev.* **1**, 286 (1937); see also J. von Neumann, *Collected Works*, A. H. Taub, Ed. (Pergamon, New York, 1962), vol. IV, pp. 205–218.
24. J. Stoustrup *et al.*, *Phys. Rev. Lett.* **74**, 2921 (1995). The upper limit $u^{(SV)}$ is also called $\|A\|_C$, the C-spectral norm of A (*7*). It is given by $u^{(SV)} = \Sigma_i\, s_i(A)s_i(C)$, where $s_i(A)$ and $s_i(C)$ are the ordered singular values of A and C, respectively.
25. The lower limit $l^{(EV)}$ is also called $\rho_C(A^\dagger)$, the C-spectral radius of $A^\dagger$ (*7*). It is given by $l^{(EV)} = \max_P |\Sigma_i\, \lambda_i(A^\dagger) \lambda_{\pi(i)}(C)|$, where P is the set of all possible permutations $\{\pi(1), \pi(2), \ldots\}$, and $\lambda_i(A^\dagger)$ and $\lambda_i(C)$ are the eigenvalues of $A^\dagger$ and C, respectively.
26. If A and C are Hermitian operators (that is, $A = A^\dagger$ and $C = C^\dagger$), the unitary bound b is identical to the C-spectral radius of $A^\dagger$, which simplifies to $l^{(EV)}{}_{herm} = \Sigma_i\, \lambda_i(A)\lambda_i(C)$, where $\lambda_i(A)$ and $\lambda_i(C)$ are the ordered eigenvalues of A and C, respectively.
27. Any unitary transformation can be implemented experimentally if the dimension of the Lie algebra, generated by the Hamiltonian H_0, the available control fields, and the identity operator is identical to the dimension of the space of all unitary operators U (*8*). Moreover, in the important case of N nondegenerate spins-$\frac{1}{2}$ arbitrarily connected by weak scalar couplings, the Pauli matrices σ_{kx}, σ_{ky}, and σ_{kz} ($k = 1, 2, \ldots, N$) plus the coupling terms $\sigma_{kz} \otimes \sigma_{lz}$ ($k < l \leq N$) generate the entire algebra $su(2^N)$ by way of commutation (the operator $\otimes$ denotes the tensor product between parts of spin spaces). Hence, every unitary transformation $UAU^\dagger$ can be generated by spin Hamiltonians as a sequence of (selective) radio-frequency pulses and delays. However, in higher spins-j with $j \geq 1$, the Pauli matrices σ_x, σ_y, and σ_z themselves no longer span the (reducible) spin-j representation of $su(2)$. Thus, in contrast to the uniquely favorable case of spins-$\frac{1}{2}$, in higher spins all multipole interactions have to be controllable as well.
28. N. C. Nielsen, T. Schulte-Herbrüggen, O. W. Sørensen, *Mol. Phys.* **85**, 1205 (1995).
29. D. P. Weitekamp, J. R. Garbow, A. Pines, *J. Chem. Phys.* **77**, 2870 (1982); P. Caravatti, L. Braunschweiler, R. R. Ernst, *Chem. Phys. Lett.* **100**, 305 (1983); S. J. Glaser and J. J. Quant, in *Advances in Magnetic and Optical Resonance*, W. S. Warren, Ed. (Academic Press, New York, 1996), vol. 19, pp. 59–252.
30. See, for example, A. Seierstad and K. Sydsæter, *Optimal Control Theory with Economic Applications* (North-Holland, Amsterdam, 1987).

31. We thank J. Jeener and W. S. Warren for helpful discussions. S.J.G. and C.G. acknowledge support by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft under grants GI 203/1-6, GI 203/2-2, and Gr 1211/6-1. T.S.-H. is indebted to R. R. Ernst for support.

15 October 1997; accepted 23 February 1998