Supporting Material for "Universal Characteristics of Chemical Synthesis and Property Optimization"

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Proof of Fitness Landscape Topology

This supplemental material presents a proof of the two main conclusions of OptiChem theory: (i) the existence of a trap-free landscape topology and (ii) the allowed presence of multiple optimal solutions (i.e., distinct "homologous" molecules, materials, or synthesis conditions that produce the same fitness value J). These two conclusions specify the corresponding predictions (a) and (c) of OptiChem theory in the main text; prediction (b) follows as a corollary. Recall that the existence of a trap-free landscape topology depends on satisfaction of the assumptions of (i) a well-posed optimization goal and (ii) no significant constraints imposed on the variables, as well as the basic consideration that synthesis is bounded by 100% yield and chemical properties generally have finite values. The derivation of the landscape topology draws on special material from convex optimization theory and quantum mechanics; appropriate references are provided for further background.

We consider a target chemical system (e.g., reagent) that interacts with a surrounding environment (e.g., solvent). Both the chemical system and environment are described quantum-mechanically; the system is referred to as being open (i.e., to the environment). The state of an open quantum system containing m accessible energy levels may be represented by an $m \times m$ density matrix ρ . In practical applications, the value of m could be very large, but the landscape analysis below holds for any finite value of m. The elements of ρ are generally complex numbers, and ρ is required to have the following properties [1]:

- i ρ is Hermitian, i.e. $\rho^{\dagger} = \rho$.
- ii $\rho \ge 0$ is a positive matrix.
- iii ρ has unit trace, $\operatorname{Tr}(\rho) = \sum_{j}^{m} \rho_{jj} = 1$.

The physical basis of these properties is as follows. Hermiticity is required to ensure that the eigenvalues of ρ are real numbers. Since quantum mechanics postulates that any observable quantity is associated with the eigenvalues of the corresponding operator, the Hermiticity requirement ensures that observables are real measurable quantities. The *j*th diagonal element ρ_{jj} is the probability of the indicated level being populated, so the positivity requirement $\rho \geq 0$ means that each probability is positive and $\text{Tr}(\rho)=1$ ensures that the probabilities sum to unity.

OptiChem theory rests on the ability to generally describe chemical transformations of open systems. The general transformation of an initial state ρ_0 (i.e., before the chemical transformation has occurred) to the state ρ (i.e., the state of the products after the chemical transformation) can be represented by a function Φ such that $\rho = \Phi(\rho_0)$. The transformation described by Φ has the properties of being trace-preserving (i.e., $\text{Tr}\Phi(\rho_0)=\text{Tr}(\rho)=\text{Tr}(\rho_0)=1$) and completely positive (CP). The trace-preservation property of Φ maintains the sum of probabilities at unity. The CP requirement ensures satisfaction of the property $\rho \ge 0$, in particular under transformation of ρ_0 to some other density matrix ρ [2, 3]. Such CP, trace preserving functions Φ are called Kraus maps, which can be uniquely determined by Kraus matrices K [2, 3].

For an open system of dimension m, the matrix K describing a Kraus map is an $m^2 \times m^2$ matrix

composed of m^2 complex $m \times m$ sub-matrices K_{ij} [3],

$$\boldsymbol{K} = \begin{pmatrix} K_{11} & \dots & K_{1m} \\ \vdots & \ddots & \vdots \\ K_{m1} & \dots & K_{mm} \end{pmatrix}.$$
 (1)

Using Eq. (1), the action of the Kraus map Φ on the initial state ρ_0 , $\Phi(\rho_0)$ produces an $m \times m$ matrix $\rho = \Phi(\rho_0)$ with elements

$$\rho_{\nu\mu} = \sum_{\sigma,\tau=1}^{m} \boldsymbol{K}_{\langle \mu\nu\rangle,\langle\sigma\tau\rangle}(\rho_0)_{\sigma\tau},\tag{2}$$

where $\langle \mu\nu \rangle = \mu + m(\nu - 1)$ and $(\mu, \nu = 1, 2, ..., m)$ and $\mathbf{K}_{\langle \mu\nu \rangle, \langle \sigma\tau \rangle}$ is the appropriate matrix element of \mathbf{K} .

The CP and trace preservation conditions imply certain constraints on the structure of the K_{ij} matrices. The CP condition of the map Φ is equivalent to the matrix positivity condition $\mathbf{K} \geq 0$. The condition of trace preservation becomes $\operatorname{Tr} K_{ij} = \delta_{ij}$ for all $i, j = 1, \ldots, m$ [3]. These two constraints imply that the collection of all possible Kraus matrices $\{\mathbf{K}\}$ for the transformation of ρ forms a *convex set*. A convex set $\{x\}$ of elements x (e.g., matrices with specific properties) has the feature that for any two members of the set, x_0 and x_1 , their *convex sum*, $x_{\lambda} = (1 - \lambda)x_0 + \lambda x_1$ for $0 \leq \lambda \leq 1$ produces x_{λ} that is in the set $\{x\}$, i.e., has all the required properties of elements in the set.

In order to show the convexity of the set $\{\mathbf{K}\}$, choose two arbitrary matrices \mathbf{K}_0 and \mathbf{K}_1 from the set of allowed Kraus matrices $\{\mathbf{K}\}$ and consider their convex sum $\mathbf{K}_{\lambda} = (1-\lambda)\mathbf{K}_0 + \lambda\mathbf{K}_1, 0 \leq \lambda \leq 1$. In order for the set $\{\mathbf{K}\}$ to be convex, the matrix \mathbf{K}_{λ} must be positive and trace-preserving, as described above. First, the sum of two positive matrices $(1-\lambda)\mathbf{K}_0$ and $\lambda\mathbf{K}_1$ must also be positive, so \mathbf{K}_{λ} satisfies the matrix positivity requirement. Second, if $(\mathbf{K}_{\lambda})_{i,j}$ denotes the (i,j) block of the matrix \mathbf{K}_{λ} , then $\operatorname{Tr}(\mathbf{K}_{\lambda})_{i,j} = (1-\lambda)\operatorname{Tr}(\mathbf{K}_0)_{i,j} + \lambda\operatorname{Tr}(\mathbf{K}_1)_{i,j} = (1-\lambda)\delta_{i,j} + \lambda\delta_{i,j} = \delta_{i,j}$, so the matrix \mathbf{K}_{λ} satisfies the trace-preservation requirement. Thus, \mathbf{K}_{λ} is in the set $\{\mathbf{K}\}$, thereby implying that the set of Kraus matrices is convex.

The convexity property of $\{K\}$ will now be combined with the physical definition of the fitness J to prove the inherent existence of trap-free landscape topology for J. Based on quantum mechanics, J is characterized by a suitable observable O, expressed as an $m \times m$ Hermitian matrix [4], such that

$$J := \operatorname{Tr}\left[\rho O\right],\tag{3}$$

where ρ is the state of the system after the chemical transformation described by the Kraus map in Eq. (2). The initial state ρ_0 of the system may be transformed through an alteration of the laboratory accessible variables p (i.e., a vector of variables $[p_1, p_2, \ldots]$ discussed in the main text). The value of the objective J then becomes

$$J = J(\mathbf{p}) = J(\mathbf{K}^{\mathbf{p}}) = \operatorname{Tr}\left[\Phi_{\mathbf{K}^{\mathbf{p}}}\rho_{0}O\right] = \sum_{\sigma,\tau=1}^{m} \mathbf{K}_{\langle\mu\nu\rangle,\langle\sigma\tau\rangle}(\rho_{0})_{\sigma\tau}O_{\nu\mu}.$$
(4)

In Eq. (4), the variables p determine the fitness J by acting on the system through the matrix K^p , where the superscript indicates that the Kraus matrix depends on the variables p. The explicit dependence of K^p upon the variables p may be complicated and determined by the particular system under study, but knowledge of this relationship is not necessary to establish the landscape topology of J(p) for OptiChem theory. The formal description of chemical transformations using the analysis below in terms of the set of Kraus matrices $\{K\}$ is general for all chemical systems and synthesis or property optimization objectives.

We can combine the convexity property of the set $\{\mathbf{K}\}$ with the inherent linear dependence of $J(\mathbf{K})$ upon \mathbf{K} (i.e., from Eq. (4)) to show that the resulting landscape J contains no local minima or maxima (i.e., traps) and that homologous optimal solutions of J may produce multiple connected regions preserving the value of J on the landscape. These properties hold regardless of the particular nature of the initial density matrix ρ_0 or the chemical objective described by the Hermitian observable operator O; the analysis only relies on J being linear in \mathbf{K} . The trap-free nature of the landscape can only be shown to hold when $\{\mathbf{K}\}$ is a convex set; constraints placed on the variables p that limit the possible Kraus matrices could make the set $\{\mathbf{K}\}$ non-convex and thereby destroy the trap-free property of the control landscape.

First, we show that the function $J(\mathbf{K})$ contains no local maxima; establishing that J contains no local minima is equivalent. Suppose that there exists a local maximum $\mathbf{K}_{(0)}$ on the landscape. This means that

- (1) There exists a neighborhood of $\mathbf{K}_{(0)}$ denoted as $U(\mathbf{K}_{(0)})$ within the convex set $\{\mathbf{K}\}$ such that for all $\mathbf{K}_{(i)}$ in $U, J(\mathbf{K}_{(i)}) \leq J(\mathbf{K}_{(0)})$ (i.e., $\mathbf{K}_{(0)}$ is a maximum).
- (2) There exists some maximum $\mathbf{K}_{(1)}$ such that $J(\mathbf{K}_{(1)}) > J(\mathbf{K}_{(0)})$ (i.e., $\mathbf{K}_{(0)}$ is not a global maximum).

Since the set $\{\mathbf{K}\}$ is convex, then $\mathbf{K}_{(\lambda)} = (1 - \lambda)\mathbf{K}_{(0)} + \lambda\mathbf{K}_{(1)}$ is in $\{\mathbf{K}\}$. Consider $J(\mathbf{K})$ to lie on the line connecting the points $\mathbf{K}_{(0)}$ and $\mathbf{K}_{(1)}$. $J(\mathbf{K})$ is a strictly monotonic function of λ , that is, $J(\mathbf{K}_{(\lambda_2)}) > J(\mathbf{K}_{(\lambda_1)})$ for any $\lambda_2 > \lambda_1$. In particular, for any $\lambda > 0$, $J(\mathbf{K}_{(\lambda)}) > J(\mathbf{K}_{(0)})$. But, if λ is small enough, we may consider $\mathbf{K}_{(\lambda)}$ to be in the neighborhood $U(\mathbf{K}_{(0)})$, which contradicts condition (1) above. Thus, \mathbf{K}_0 cannot be a local maximum; only global maxima exist on the landscape. Importantly, this argument only holds when $\{\mathbf{K}\}$ is a convex set.

A "solution" to a posed chemical synthesis or property goal is specified abstractly here by the Kraus transformation \mathbf{K} . The convexity of the set $\{\mathbf{K}\}$ also results in the homologous solutions of $J(\mathbf{K})$ (i.e., solutions with the same J value) being connected. To see this property, let $\mathbf{K}_{(0)}$ and $\mathbf{K}_{(1)}$ be two homologous solutions, i.e., $J(\mathbf{K}_{(1)}) = J(\mathbf{K}_{(0)})$. Thus, we have that $J(\mathbf{K}_{(\lambda)}) = (1 - \lambda)J(\mathbf{K}_{(1)}) + \lambda J(\mathbf{K}_{(0)}) = (1 - \lambda + \lambda)J(\mathbf{K}_{(0)}) = J(\mathbf{K}_{(0)})$, for all $\lambda \in [0, 1]$, so any point on the segment connecting $\mathbf{K}_{(0)}$ and $\mathbf{K}_{(1)}$ is also a homologous solution, implying that the homologous solutions are connected.

To summarize, the following landscape properties were shown to hold in terms of a general chemical transformation \mathbf{K} : (i) for any initial density matrix ρ_0 and any physical observable O, the function $J(\mathbf{K}) = \text{Tr}[\sum_{i,j} K_{ij}\rho_0 O]$ does not have local minima or maxima and (ii) connected optimal homologous solutions exist. In order for the same landscape topology to hold in terms of the laboratory variables \mathbf{p} , the conditions of a well-posed objective and sufficiently unconstrained variables discussed in the main text must be satisfied. Furthermore, the connectivity of optimal homologous solutions may not hold if practical constraints on the variables \mathbf{p} reduce the set of reachable optimal transformations to possibly multiple isolated sets of Kraus matrices.

References

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