Entropy Maximizations on Electron Density *

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Incomplete and imperfect data characterize the problem of constructing electron density representations from experimental information. One fundamental concern is identification of the proper protocol for including new information at any stage of a density reconstruction. An axiomatic approach developed in other fields specifies entropy maximization as the desired protocol. In particular, if new data are used to modify a prior charge density distribution without adding extraneous prejudice, the new distribution must both agree with all the data, new and old, and be a function of maximum relative entropy. The functional form of relative entropy is $\sigma = -\varrho \ln(\varrho/\tau)$, where ϱ and τ respectively refer to new and prior distributions normalized to a common scale.

Entropy maximization has been used to deal with certain aspects of the phase problem of X-ray diffraction. Varying degrees of success have marked the work which may be roughly assigned to categories as direct methods, data reduction and analysis, and image enhancement. Much of the work has been expressed in probabilistic language, although image enhancement has been somewhat more physical or geometric in description. Whatever the language, entropy maximization is a specific and deterministic functional manipulation. A recent advance has been the description of an algorithm which, quite deterministically, adjusts a prior positive charge density distribution to agree exactly with a specified subset of structure-factor moduli by a constrained entropy maximization.

Entropy on an N-representable one-particle density matrix is well defined. The entropy is the expected form, and it is a simple function of the one-matrix eigenvalues which all must be non-negative. Relationships between the entropy functional and certain properties of a one-matrix are discussed, as well as a conjecture concerning the physical interpretation of entropy. Throughout this work reference is made to informational entropy, not the entropy of thermodynamics.

Key words: Charge density; Correlation energy; Density matrix; Entropy maximization; Hohenberg-Kohn theorem.

1. Introduction

Entropy, like the die so often invoked in its discussion, has many faces. Although its functional form is the same in thermodynamics and information physics, in this work there is no further consideration of thermodynamic entropy. The term entropy in connection with information and the work of Shannon (vid. Shannon and Weaver [1]) is actually something of an accident. When he found a well-behaved measure of uncertainty associated with a probability distribution for n outcomes, Shannon considered calling it information or uncertainty, but John v. Neumann persuaded him to call it entropy. Whatever good reasons there may be for a parallel, or, in certain cases, even an equivalence between information measures and thermodynamics, von Neumann's were focused on limiting to one the names of the functional form (Denbigh and Denbigh [2]).

Some notable uses of informational entropy are in spectral factorization or autocorrelation deconvolution, analysis of communications networks, analysis of populations and probabilities for a wide range of practical problems, image enhancement and reconstruction, and a logic of consistent inference. These and other applications provide forms immediately adaptable to many crystallographic problems. But the predominant crystallographic use of informational entropy is in the extraction of optimal electron density functions from diffraction data, and the present discussion will be limited to various aspects of this general phase problem of X-ray diffraction.

The language of probability and statistics was not used in the first applications of entropy maximization to determination of an electron density function (Collins [3, 4]), and in this paper it will be used only incidentally. In contrast, probabilistic concepts were a critical part of the antecedent work of Gull and Daniell [5], and they played an important rôle in much

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of the early crystallographic discussion of entropy maximization (Wilkins, Varghese, and Lehman [6], Navaza, Castellano, and Tsoucaris [7], Bricogne [8]), and continue to do so (e.g., Bricogne [9], MacLachlan [10], Gilmore, Henderson, and Bricogne [11, 12]). The viewpoint of the present discussion is that of the general phase problem as a physical problem, in order to emphasize the physical nature of charge density.

The common presumption of a (nonphysical) uniform distribution of atoms in a unit cell insufficiently constrains entropy maximization and other known direct methods for phasing structures of substantial complexity, or perhaps one should say, phasing data sets of limited resolution. On the probabilistic side, immediate advantage is expected from a better distribution of atoms, and Bricogne, in his papers, has emphasized moving away from the uniform distribution to updated, physically realistic, non-uniform distributions expressed in the joint distribution of structure factors. On the physical side, more deterministic constraints are sought for charge density, and here the search is in the direction of a quantum-mechanically informed entropy maximization.

Initially, a heuristic foundation is given for use of entropy in the physical context, and straightforward development leads to some applications. Then a quantum-mechanically structured formalism is given for entropy maximization on a density matrix. Finally, a conjecture is made concerning physical interpretation of entropy on a one-particle density matrix.

2. Entropy

Given a set of possible events each with a probability p_i, Shannon [1] posed the problem of finding a measure of how much "choice" is involved in the selection of an event, or of the uncertainty of a particular outcome. This is the problem solved by Shannon's entropy, or just entropy. Fougere [13] set out Shannon's desiderata or axioms in the following form. If S is the measure of uncertainty:

1. $S = S(p_1, p_2, \ldots, p_n)$. The information depends upon the entire set of probabilities.
2. If all p_i are equal, then S is a monotone increasing function of n. With more possibilities to choose from, the information in a choice is greater.
3. S is additive for compound independent events. If events A and B are independent, $S(AB) = S(A) + S(B)$.
4. S does not depend upon how the problem is set up. For example,

$$S\left(\frac{1}{2},\frac{1}{6},\frac{1}{3}\right) = S\left(\frac{1}{2},\frac{1}{2}\right) + \frac{1}{2}S\left(\frac{1}{3},\frac{2}{3}\right).$$

The intermediate state corresponding to the rightmost term occurs with probability $\frac{1}{2}$ and is so weighted. That is, the information in the probability assignment $A = \frac{1}{2}$, $B = \frac{1}{6}$, $C = \frac{1}{3}$, must be the same as in the assignment $A = \frac{1}{2}$, $D = \frac{1}{2}$, with resolution of intermediate state D by probability assignment $B = \frac{1}{3}$, $C = \frac{2}{3}$.

Shannon showed that, within a positive factor,

$$S = -\sum_i p_i \ln p_i, \tag{1}$$

and that only this functional form, now associated with his name, satisfies the assumptions.

Shore and Johnson [14] established the uniqueness of the entropy functional in an especially useful way. They showed that if new data were used to modify a prior distribution without adding extraneous prejudice, then the new distribution must both agree with all the data, new and old, and be a function with maxium relative entropy having the form

$$\sigma = -\varrho \ln(\varrho/\tau). \tag{2}$$

This established consistent inference as a requirement sufficient to determine the entropy formula.

The most general statement of the outcome of Shore and Johnson's [14] axioms is given by Skilling [15]. Skilling abandons the limitation of dealing with probability distributions and considers positive (not necessarily normalized) distributions in general. The problem posed is to devise a ranking scheme by which to order images reconstructed from observational information. The ranking is to consist in assigning a number S to each image f, such that for any pair of images the better has a greater S. An acceptable form of S is determined by the satisfaction of four assumptions or axioms which Skilling summarizes informally in statements of their justification. The substance of his informal statements is:

Axiom I. *Subset independence.* Information about one domain of an image should not affect the reconstruction in a different domain, provided there is no constraint directly linking the domains.

Axiom II. *Coordinate invariance.* The same answer is expected when the same problem is solved in

two different coordinate systems, in that the reconstructed images in the two systems should be related by the coordinate transformation.

Axiom III. *System independence.* If all that is known about an image f is its (independent) marginal distributions a_1 and a_2, the recovered image is to be, within a positive constant factor, the uncorrelated reconstruction $f = a_1 a_2$. Any other choice of f would imply correlation for which there is no evidence.

Axiom IV. *Scaling.* In the absence of any additional information, the initial measure of the image is to be recovered. If all that is known about a simple well behaved function is its mean, any acceptable reconstruction must have the same mean.

In consequence of these axioms, there is an entropic regularization formula to be maximized when selecting an optimal image f. The same form arises in a parallel analysis for selection of a prior model m, and Skilling combines them, in the discrete case, in the entropy form

$$S = \sum_i [f_i - m_i - f_i \ln (f_i/m_i)], \tag{3}$$

which can be used to rank and select image-model pairs.

In the present context, charge density ϱ is an image, and its prior model τ will often be taken as the uniform distribution corresponding to the correct electron count. S has certain interesting properties conceptually useful in the discussion of charge density distribution.

1. $S = 0$ is a global maximum achieved when ϱ and τ coincide. The decrease of S from its global maximum is a measure of the deviation of ϱ from its prior model τ.
2. Relative to a prior uniform distribution, any change which preserves $\sum_i \varrho_i$ and diminishes $\sum_i \varrho_i^2$ will increase S; the flatter the density, the greater its entropy (Collins and Prince [16]).
3. Equation (1) is the form suitable for ranking sets of spatially unrelated nonnegative numbers normalized to a fixed but arbitrary scale, e.g., a set of probabilities; its global maximum and minimum are achieved, respectively, when all members of a set are equal, and when all members but one are zero.

3. Entropy, Exponential Density, and Structure Factor Fitting

There is a continuing need for methods to construct optimal charge density functions from available data. A substantial advance was made with the introduction of direct entropy maximization on the charge density to the crystallographic literature (Collins [4]), and with the demonstration of its corresponding implied exponential representation as a competent model (Collins and Mahar [17]). The intent of that work was to obtain, for biological macromolecules, optimal density maps based on the imperfect data characteristic of X-ray diffraction experiments. Constrained entropy maximization and the consequent exponential model of density necessarily yield positive-definite results. Other favorable results shown in various simulations include partial defeat of series termination error, improvement of initial phase assignments, resolution enhancement, and opportunity for proper handling of information in addition to the Fourier coefficients of density. An example of the possible accuracy and precision of entropy maximization on density is given elsewhere in this volume by Takata, Kubota and Sakata [18].

The formalism first presented by Collins [4] led to an algorithmic application conveniently described as iterative adjustment of the logarithm of density to improve the agreement between observed and calculated structure factors. The reconstruction procedure was based on

$$\varrho_k = \exp\Big[\ln \tau_k + \sum_j \theta_j [F_o(\boldsymbol{h}_j) - F_c(\boldsymbol{h}_j)] \exp[-2\pi i \boldsymbol{h}_j \cdot \boldsymbol{r}_k]\Big], \tag{4}$$

where ϱ_k is the current iterate of charge density sampled at $\boldsymbol{r}_k$, τ_k is the corresponding prior model sample, θ_j is a collection of constants that weight and scale the difference density coefficient, and $F_c(\boldsymbol{h}_j)$ is the Fourier transform of τ sampled at reciprocal lattice vector $\boldsymbol{h}_j$, corresponding to the observed structure modulus $|F_o(\boldsymbol{h}_j)|$; the phase angle assigned to $|F_o|$ can be held at its initial value or updated for each iteration. A successful outcome for this reconstruction procedure depends on the use or discovery of a good model. For problems at atomic resolution or better, the procedure is quite generally an excellent means for adjusting a positive-definite density to bring it into closer agreement with observed structure moduli. It is fast and stable, and in the case of abundant accurate data, it

can be used to generate an unambiguous solution to the phase problem.

Sjölin, Prince, Svensson, and Gilliland [19] used a dual method to find a complete solution to the problem of exactly fitting structure moduli given initial estimates of their phases. This may be stated as a standard nonlinear programming problem (Collins and Prince [16]) in the form

$$\text{maximize} \sum_i \sigma_i, \tag{5a}$$

$$\text{subject to } \mathbf{G}_c(\mathbf{a}) - \mathbf{G}_o = \mathbf{0}, \tag{5b}$$

where the entropy of a density map is to be maximized, $\mathbf{G}_c(\mathbf{a})$ is a vector of structure moduli $|F_c(\boldsymbol{h}_j)|$ obtained from Fourier inversion of the map, $\mathbf{G}_o$ is the corresponding vector of observations $|F_o(\boldsymbol{h}_j)|$, and $\mathbf{a}$ is a vector of multipliers to be determined. With respect to ϱ_i, maximization of

$$Q = \sum_i \sigma_i + \mathbf{a}^\dagger [\mathbf{G}_c(\mathbf{a}) - \mathbf{G}_o] \tag{6}$$

yields the dual function

$$\zeta(\mathbf{a}) = \text{maximum}\left[\sum_i \sigma_i + \mathbf{a}^\dagger [\mathbf{G}_c(\mathbf{a}) - \mathbf{G}_o]\right], \tag{7}$$

to be optimized in an unconstrained minimization with respect to $\mathbf{a}$. The uniform density is used as the model function, and

$$|F_c(\boldsymbol{h}_j)| = \sum_i \varrho_i \cos[2\pi \boldsymbol{h}_j \cdot \boldsymbol{r}_i - \alpha(\boldsymbol{h}_j)], \tag{8}$$

where α is the phase associated with $|F_c|$. At the maximum of Q,

$$\varrho_k = \exp\left[\sum_j \alpha_j \cos[2\pi \boldsymbol{h}_j \cdot \boldsymbol{r}_k - \alpha(\boldsymbol{h}_j)]\right], \tag{9}$$

the final expression for a positive-definite exponential model of density.

The solution of (5) is completed by minimization of $\zeta(\mathbf{a})$ by a Newton method to evaluate the elements of $\mathbf{a}$. After l iterations, this gives the vector of multipliers as

$$\mathbf{a}_l = \mathbf{a}_{l-1} - \mathbf{H}[\zeta(\mathbf{a})]^{-1} \nabla \zeta(\mathbf{a}), \tag{10}$$

for which the gradient ∇ and an approximation to the Hessian matrix $\mathbf{H}$ of ζ are needed. The gradient of ζ has the notably simple form

$$\nabla \zeta(\mathbf{a}) = \mathbf{G}_c(\mathbf{a}) - \mathbf{G}_o. \tag{11}$$

Because the system of equations to be solved is likely very large, it may be desirable to use quasi-Newton methods, or the truncated-Newton methods (Nash [20]) recently shown to be especially effective (Decarreau, Hilhorst, Lemaréchal, and Navaza [21]), and these methods can build an approximation to the Hessian matrix of ζ without its direct computation. It is important to recognize that the Hessian matrix is positive-definite [16, 19]. If for an initial phase assignment a solution to (5) exists, then it is unique.

Prince's method, in spite of being similar in appearance to much antecedent work, is a profound departure from prior related analyses. Specifically, Prince's method is the first to use as constraints only modulus information in the computation of an exponential density. That is, although initial phase assignments are used, phases are fixed and not adjustable parameters of the optimization. (In practice, bad choices are occasionally made for phases, and implementation must allow for alternate choices in these cases.) The difference between Prince's method and others is emphasized by their multipliers. Prince's multipliers a_j are real, and, e.g., those of Lemaréchal and Navaza [22] are complex, as are those of Bricogne [8], which, though real, are in the ordered pairs commonly represented as complex variables. It should be noted that Prince's method, although it can be used in solution of the phase problem, is here referred to only in its algorithmic sense of finding the map of maximum entropy that can be inverted to yield exact magnitudes for a subset of moduli which have been assigned phases.

4. Entropy on a Density Matrix

For many years it has been known that the ordinary electron density function of crystallography is a contraction of the fully elaborated quantum-mechanical representation of an electronic ground state (vid. McWeeny and Sutcliffe [23]). It will be clear that in this section the discussion refers to a state of idealization hopelessly beyond reach of protein crystallography. Nevertheless, the power and success of entropy maximization on ordinary charge density suggests that entropy maximization in the context of a more general underlying reality may unveil additional power for dealing with the phase problem.

The sufficient information for one-electron properties, among which is charge density, is carried by the one-electron, or one-particle density matrix for a system. Schmider, Smith and Weyrich [24] give a good summary of the relationship between quantum chemistry and crystallography. They begin with an N-elec-

tron wavefunction Ψ, which is formed with itself into a dyadic product, and contract the product to a one-particle reduced density matrix, or one-matrix, $\gamma(1,1')$, where the number 1 stands for the four space-spin coordinates of electron one. It is to be noted that by this construction the density matrix is N-representable, that is, there exists an N-particle dyadic product based on a many-particle wave function of correct properties, whose contraction is the one-matrix. The corresponding spin-free or spin-traced one-matrix is $\varrho(\boldsymbol{r},\boldsymbol{r}')$, and its so-called diagonal is that portion for which $\boldsymbol{r}=\boldsymbol{r}'$, and $\varrho(\boldsymbol{r},\boldsymbol{r})=\varrho(\boldsymbol{r})$, the ordinary charge density. (From here on the notions "density matrix" and "one-matrix" are used interchangeably in the sense of the latter, with and without spin.)

Here the useful forms for a one-matrix are either the eigenvalue equations

$$\gamma(1,1')=\sum_{j=1}^{\infty} n_j \chi_j(1)\chi_j^*(1'), \tag{12a}$$

where the eigenvalues n_j are the occupation numbers of the natural spin orbitals χ_j, and

$$\varrho(\boldsymbol{r},\boldsymbol{r}')=\sum_{l=1}^{\infty} n_l \psi_l(\boldsymbol{r})\psi_l^*(\boldsymbol{r}'), \tag{12b}$$

in which an eigenvalue n_l is the occupation number of (spin-free) natural orbital ψ_l, or an expansion in the orthogonal basis functions ϕ_i,

$$\varrho(\boldsymbol{r},\boldsymbol{r}')=\sum_{i,k} P_{ki}\,\phi_i(\boldsymbol{r})\,\phi_k^*(\boldsymbol{r}'). \tag{13}$$

For a one-matrix γ (representing a fermion system) to be N-representable, it suffices that the one-matrix has eigenvalues which sum to N and lie in the range $[0,1]$ (Coleman [25]). In the case of the spin-traced one-matrix ϱ, the required eigenvalue range becomes $[0,2]$; the eigenvalues must again sum to N.

For the entropy on a density matrix, Jaynes [26] has given the form

$$S=-\operatorname{tr}[\varrho(\boldsymbol{r},\boldsymbol{r}')\ln\varrho(\boldsymbol{r},\boldsymbol{r}')], \tag{14}$$

the trace of the matrix, which may be computed as

$$S=-\sum_{j=1}^{\infty} n_j \ln n_j\,{}^{+}, \tag{15}$$

+ Differing scales for n_j lead to values of S differing by a constant. Certain of Jaynes' inequalities show that his commonly used unit-normalization is not an essential feature of the eigenvalue equation for entropy. For a spin-traced singlet system with eigenvalues in the range $[0,2]$, $S=-\sum_j n_j \ln(n_j/2)$ is the entropy that properly accounts for the spin-tracing; the entropy arising from creation of two natural spin orbitals from one natural orbital is $-\ln(1/2)$.

where the eigenvalues n_j are those of (12). Evidently, entropy on an N-representable fermion one-matrix is well defined and can be calculated.

Rearrangement of

$$\varrho(\boldsymbol{r})=\frac{1}{V}\sum_i F(\boldsymbol{h}_i)\exp[-2\pi i\,\boldsymbol{h}_i\cdot\boldsymbol{r}], \tag{16}$$

the Fourier synthesis of charge density, is one way to construct a density matrix with explicit reference to structure factors. For a crystal unit cell of volume V, define

$$T_{ik}\equiv T_{\boldsymbol{h}_i-\boldsymbol{h}_k};\ \xi_i(\boldsymbol{r})\equiv V^{-1/2}\exp[-2\pi\,\boldsymbol{h}_i\cdot\boldsymbol{r}]. \tag{17}$$

Then, if by any assignment

$$\sum_{\boldsymbol{h}_i-\boldsymbol{h}_k=\boldsymbol{h}} T_{ik}\equiv\mathscr{F}(\boldsymbol{h},\mathbf{T})=F_{\boldsymbol{h}}, \tag{18}$$

$$\varrho(\boldsymbol{r},\boldsymbol{r}')=\sum_{ik} T_{ik}\,\xi_i(\boldsymbol{r})\,\xi_k^*(\boldsymbol{r}') \tag{19}$$

is a full density matrix carrying the charge density as its diagonal, provided that experimental $|F_{\boldsymbol{h}}|$ has been correctly phased. Clearly, because the elements T_{ij} are restricted only to satisfy (18), (19) cannot be expected to give the true density matrix without additional constraint. If assignment of values for $\mathbf{T}$ is additionally required to give a density matrix with nonnegative eigenvalues, then the entropy is well defined, both on a density matrix and on the charge density itself, so long as it also is nonnegative.

Macromolecular crystallography involves, for its smaller structures, unit cells containing tens of thousands of electrons. For these cases computationally tractable number representations of density matrices are not likely to substantially exceed a rank of 10^3 in $\mathbf{T}$. Of course if the rank of $\mathbf{T}$ is an order of magnitude smaller than the number of electrons in a unit cell, the eigenvalues of $\mathbf{T}$, which must sum to N, will violate their N-representability upper bound, and (19) can only be an approximation. Even so, if value assignments in $\mathbf{T}$ are governed by maximization of the entropic regularization formula, and are constrained by $\mathscr{F}(\boldsymbol{h},\mathbf{T})=F_{\boldsymbol{h}}$, the approximate density-matrix diagonal will suffer only the usual imperfections of data limitation, and the eigenvalues will be as nearly equal as possible.

5. Physical Interpretation of Entropy: A Conjecture

Entropy on a density matrix is a particularly simple functional in that it involves only eigenvalues. A one-

matrix representation of independent or uncorrelated fermions is characterized by idempotence, and its eigenvalues must therefore be 0 or 1. In quantum-mechanical calculations for real chemical systems, inspection shows the eigenvalue spectrum to change in ways that increase the entropy of the one-matrix, as electron correlation is accounted for, and it is evident that the eigenvalues carry information about the correlation.

Reconstruction of a one-matrix requires constraint beyond mere agreement with a set of (phased) structure factors. The maximization of entropy is an additional constraint, but it does not have certain claim on physical significance. Electron correlation is a physical phenomenon and the correlation energy is functionally related to the eigenvalues or occupation numbers n_j. If correlation energy is defined as

$$E_{\text{cor}} = E_0 - E^{\text{HF}} \leqq 0, \tag{20}$$

where E_0 is the true ground-state energy and E^{HF} is the Hartree-Fock or independent-particle energy, its maximum is zero and corresponds to an independent-particle state. Such a state is equally well characterized by a zero of entropy on the one-matrix.

Correlation energy and entropy on a one-matrix have, with a sign reversal, the same qualitative sense of change as eigenvalues change. It would be desirable to link the two in a definite relationship involving the eigenvalues. If a functional $\mathscr{Z}$ is to be usefully related to the correlation energy, it may be required to share some of the correlation energy's properties. The properties required here are

1. If there is a $\mathscr{Z}$, it must depend on the entire set of eigenvalues n_j; $\sum_j n_j = N$.
2. If there is a $\mathscr{Z}$, it must decrease as the measure of departure from idempotence $\sum_j (n_j - n_j^2)$ increases from zero.
3. If there is a $\mathscr{Z}$, it must allow partitioning of eigenvalues in sets following the pattern $\Gamma = \Gamma_1 \cup \Gamma_2$, for which $\mathscr{Z}(\Gamma) = \mathscr{Z}(\Gamma_1) + \mathscr{Z}(\Gamma_2)$. This is to reflect the known utility of partitioning orbital sets, and distinguishing shells and principal energy levels for computational approximation.
4. If there is a $\mathscr{Z}$, it must allow subsequent elaboration of an orbital following, for a two-particle example, the pattern

$$\mathscr{Z}(0.9, 0.8, 0.2, 0.1) = \mathscr{Z}(0.9, 0.8, 0.3) + 0.3\,\mathscr{Z}(0.33, 0.67).$$

This is to reflect the change in correlation energy as the appropriately weighted addition of correlation energy arising from the subsystem in the course of its creation.

The form of $\mathscr{Z}$ is definite and unique as discussed in paragraph 2. It is, of course, with sign reversed, the functional form of entropy, and the conjecture is that the four properties are indeed properties of electron correlation energy, thus establishing

$$E_{\text{cor}} = \varkappa \sum_j n_j \ln n_j, \tag{21}$$

where $\varkappa$ is a positive constant to be determined. Then a physical interpretation of entropy on a density matrix is that it is proportional to the negative of correlation energy.

6. Conclusion

Entropic regularization formulas have proven to be powerful tools in dealing with the phase problem. In the past decade, there have been numerous reports of structure solutions aided by entropy maximization. There also have been several reports of structures solved on the basis of entropy maximization. In a certain sense these have been special cases, e.g., small structures of few atoms, small structures with unusually large and accurate data sets, structures with special delimiting features readily identified on the basis of few phased reflections, or simulated solutions of known structures. The largest problem currently solved by entropy maximization methods is a simulation of the structure solution of recombinant bovine chymosin, a protein of 323 amino-acid residues [19]. In spite of the various reported successes, additional constraint is desireable to increase the productivity of entropy maximization algorithms.

Direct methods began as algebraic exploitation of the positivity of charge density, and were given an enduring foundation through elaboration of consequent inequality relationships among structure factors (Karle and Hauptman [27]). Exponential density is a feature of entropy maximization and imposes on charge density the requirement of positivity. Density matrices are quantum-mechanically specialized representations that can carry positive charge density as well as other information true of an electronic system. Entropy on density matrices has been presented in the hope of discovering additional power for phase determination and enhancement of charge density images,

especially for biological macromolecules. It also seems reasonable that entropic regularization will provide added control to the reconstruction of density matrices using information from diverse sources.

Entropy on density matrices brings two propositions to a need for resolution. The propositions are a principle and a theorem, both of which continue to be controversial in some ways, but also continue to stand against challenge. They are Jaynes' maximum entropy principle (JMEP, Jaynes [28]), and the Hohenberg-Kohn theorem (HKT, Hohenberg and Kohn [29]). An informal summary of the HKT (see also Berrondo and Goscinski [30] for a stronger statement in terms of the density matrix) is that charge density alone suffices to delimit the ground state of a nondegenerate electronic system fully. Similarly, JMEP is that a maximum-entropy distribution is maximally noncommittal to all matters other than satisfaction of given constraints. If in the present context both propositions are applicable, then entropy maximization on a one-matrix in agreement with charge density should suffice to determine the one-matrix. If this is true, entropy regularization formulas provide the connection implied by HKT between diagonal and off-diagonal portions of a one-matrix. Moreover, if true, this connection is unusually well suited to computational application. On the other hand, if information in addition to charge density is required to constrain entropy maximization in the reconstruction of one-matrices, JMEP assures that the needed additional information or constraint is not more than the essential minimum.

Decision of the conjecture given as (21) will be important whatever the resolution of JMEP and HKT. If it is correct, the conjecture points the way to deeper physical understanding of the rôle of one-matrices in representing electronic systems. Even if it is incorrect, the decision likely can be made only by further illuminating the relationship between the eigenvalue spectrum of a one-matrix and the correlation structure of the electronic system it represents.

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