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Electron correlation and the eigenvalues of the one-matrix

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The Jaynes entropy of the one-particle reduced density matrix is examined within the context of the convex set of N-representable one-matrices. The monotonic relationship of the Jaynes entropy with distance from the hull of the convex set is highlighted, and we show that the Jaynes entropy is monotonically related to the density-functional definition of the correlation energy, thus qualifying a conjecture of Collins which assumed a simple proportionality. It is further suggested that maximization of the Jaynes entropy subject to the constraints of fixed density and kinetic energy picks out the true one-matrix.

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I. INTRODUCTION

The centrality of the ground-state electron density in quantum chemistry is emphasized by density-functional theory and enshrined in the original Hohenberg-Kohn Theorem [1]. Formally, knowledge of the ground-state one-particle electron density $\rho_o(\mathbf{r})$ infers knowledge of *all* properties exactly, notwithstanding the current lack of knowledge of how precisely to go about determining them directly. An additional factor of interest with regard to the electron density is that it can be experimentally determined from x-ray diffraction by single crystals [2]. While this fact is well known, the measured function is related to the Fourier transform of the time-averaged electron density in the crystal, including thermal motion of the nuclei. The density-functional theory applies to a static electron density, but an approximate separation of the thermal motion using the adiabatic approximation [3] yields a quasi-Born-Oppenheimer density, which is assumed to be close enough to the static density of the same system. Given such an experimental density, it is obviously desirable to extract as much useful information as possible from it. The elucidation of effective potentials, noninteracting kinetic energies, and Kohn-Sham orbitals for a given density has been well investigated in the past [4–24].

For the electron density of a ground state, nondegenerate wave function, the noninteracting kinetic energy $T_s[\rho]$ has been shown by Lieb [25] to be unique and well defined. It can be obtained from the knowledge of the density alone by searching over all N-representable one-matrices yielding the required density and choosing the one minimizing the expectation value of the kinetic energy. Since this process is the minimization of a linear functional on a convex set, the optimal value occurs at the extreme points of that set, which are those one-matrices corresponding to determinantal wavefunctions.

The true one-matrix $\gamma_o(\mathbf{x},\mathbf{x}')$ yielding T_o and ρ_o does not correspond to a determinantal wave function and since the mapping from $\rho(\mathbf{r})\mapsto\gamma(\mathbf{x},\mathbf{x}')$ is one to many, there is no direct method of determining the true one-matrix corresponding to $\rho_o(\mathbf{r})$. In the following section, we highlight the topological properties of the set of N-representable one-matrices emphasizing the convexity of this set. There has been interest in the eigenvalue structure $\{n_i\}$ of the one-matrix, in particular its Jaynes entropy [26]

$$S_J=-\sum_i n_i \ln n_i\,. \tag{1.1}$$

We highlight some interesting properties of this *concave* functional and show it to be a monotonically increasing function of a well-defined distance measure from the convex hull. Using relations derived by Savin [27] and Levy and Görling [28], we provide a modification of Collins' conjecture [29] that the Jaynes entropy is proportional to the correlation energy, by using a definition of the correlation energy from the density functional theory and show that for this definition, the entropy is a monotonically increasing function of the correlation energy.

Finally, we provide a conjecture of our own which states that given the true ground-state density and the true kinetic energy, we can reconstruct the true one-matrix by the application of the Jaynes maximum-entropy principle.

II. CONVEXITY OF FERMION DENSITY MATRICES

For a system of N particles, the pure state N-particle density matrix is defined as the integral projection operator with kernel

$$\begin{aligned}\Gamma_k^N(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N;\mathbf{x}_1',\mathbf{x}_2',\ldots,\mathbf{x}_N')\\ =\Psi_k(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N)\Psi_k^*(\mathbf{x}_1',\mathbf{x}_2',\ldots,\mathbf{x}_N')\end{aligned} \tag{2.1}$$

with $\mathbf{x}=(\mathbf{r},\sigma)$ and where the $\Psi_k(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N)$ form a complete orthonormal set of antisymmetric N-particle wave functions. Γ_k^N has the properties of Hermiticity ($\Gamma^\dagger=\Gamma$), non-negativity ($\Gamma\geqslant 0$) and idempotency ($\Gamma^2=\Gamma$). This definition may then be generalized to define *ensemble* N-particle density matrices

$$\begin{aligned}\Gamma^N(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N;\mathbf{x}_1',\mathbf{x}_2',\ldots,\mathbf{x}_N')\\ =\sum_k W_k\Psi_k(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N)\Psi_k^*(\mathbf{x}_1',\mathbf{x}_2',\ldots,\mathbf{x}_N')\\ =\sum_k W_k\Gamma_k(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N;\mathbf{x}_1',\mathbf{x}_2',\ldots,\mathbf{x}_N')\end{aligned} \tag{2.2}$$

with $W_k \geqslant 0$ and $\Sigma_k W_k = 1$.

The set of all ensemble N-particle density matrices $\{\Gamma^N\}$ is denoted by $\mathcal{P}^N$. This is obviously a convex set in the sense that if $A,B \in \mathcal{P}^N$ then $aA + bB \in \mathcal{P}^N$ for all $a,b \geqslant 0$ and $a + b = 1$. C is an extreme point of the set if $C = aA + bB$ implies that A and B are multiples of C and therefore the extreme points of $\mathcal{P}^N$ are pure states, and are characterized by the idempotency condition.

The Klein-Milman theorem asserts that a convex set is determined by its extreme points, all other elements being obtained by linear combination and hence the convex set is the convex closure of that set's extreme points. This leads to the interpretation of the convex set $\mathcal{P}^N$ topologically as a cone or convex hull [30–34].

In quantum chemistry the Hamiltonian contains, at most, two-particle interactions and in this sense the N-particle density operator contains more details than necessary. In this work we concentrate on the one and two-particle *reduced* density matrices γ and Γ defined by the action of the contraction operator [33]

$$\begin{aligned}\gamma(\mathbf{x},\mathbf{x}') &= \mathcal{L}_N^1 \Gamma^N(\mathbf{x},\mathbf{x}_2,\ldots,\mathbf{x}_N;\mathbf{x}',\mathbf{x}_2,\ldots,\mathbf{x}_N)\\ &= \int \cdots \int \Gamma^N(\mathbf{x},\mathbf{x}_2,\ldots,\mathbf{x}_N;\mathbf{x}',\mathbf{x}_2,\ldots,\mathbf{x}_N)\\ &\quad \times d\mathbf{x}_2,\ldots,d\mathbf{x}_N \end{aligned} \tag{2.3}$$

$$\begin{aligned}&\Gamma(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2')\\ &\quad = \mathcal{L}_N^2 \Gamma^N(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N;\mathbf{x}_1',\mathbf{x}_2',\ldots,\mathbf{x}_N)\\ &\quad = \int \cdots \int \Gamma^N(\mathbf{x}_1,\mathbf{x}_2,\ldots,\mathbf{x}_N;\mathbf{x}_1',\mathbf{x}_2',\ldots,\mathbf{x}_N)\\ &\qquad \times d\mathbf{x}_3,\ldots,d\mathbf{x}_N \end{aligned} \tag{2.4}$$

and related to each other by

$$\gamma(\mathbf{x},\mathbf{x}') = \mathcal{L}_2^1 \Gamma(\mathbf{x},\mathbf{x}_2;\mathbf{x}',\mathbf{x}_2'). \tag{2.5}$$

In order to obtain the energy of the system, the reduced Hamiltonian, $\hat{K}$ acts on the three-variable function

$$E = \mathrm{tr}[\hat{K}\Gamma(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2)], \tag{2.6}$$

however this can be partitioned into one- and two-particle terms

$$\hat{K} = \hat{H}^1 + \hat{H}^2, \tag{2.7}$$

where the one-particle term contains kinetic and nuclear-electron components

$$\hat{H}^1 = N(\hat{T} + \hat{V}_{ne}) \tag{2.8}$$

and acts on the one-matrix to give the one-particle energy

$$E^1 = \mathrm{tr}[\hat{H}^1 \gamma(\mathbf{x},\mathbf{x}')], \tag{2.9}$$

and the two-particle term contains the electron-electron term

$$\hat{H}^2 = \frac{N(N-1)}{2}\hat{V}_{ee} \tag{2.10}$$

acting on the diagonal of the two-matrix to give the two-particle energy

$$E^2 = \mathrm{tr}[\hat{H}^2 \Gamma(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1,\mathbf{x}_2)]. \tag{2.11}$$

We take $\gamma(\mathbf{x},\mathbf{x}')$ and $\Gamma(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2')$ to be normalized to unity, although other values are also common [35,36]. Since γ has been obtained by contraction of an N-particle ensemble density operator, it is termed *ensemble N* representable, and is a member of the set $\mathcal{P}_N^1$. This set is a subset of $\mathcal{P}^1$, the set of all positive [37], Hermitian one-particle density operators of unit trace including those where γ cannot be obtained by the above contraction mapping, i.e., no Γ that contracts to the given γ exists. Expressing the one-matrix in terms of its spectral resolution

$$\gamma(\mathbf{x},\mathbf{x}') = \sum_i n_i \phi_i(\mathbf{x}), \phi_i^*(\mathbf{x}'), \tag{2.12}$$

the necessary and sufficient conditions that γ must satisfy to be a member of the set $\mathcal{P}_N^1$ are (i) that its eigenvalues, n_i lie on the interval $[0,1/N]$ and (2) that Tr $\gamma = \Sigma_i n_i = 1$ [38].

Since $\mathcal{P}^N$ is convex and the contraction $\mathcal{L}_N^1$ is a linear map, the set $\mathcal{P}_N^1$ is also convex, and is again specified by knowledge of its extreme points, which in this case are those one-matrices having N eigenvalues equal to $1/N$ and all others zero that we denote as $\{\gamma_{\mathrm{I}}\}$. These satisfy $N\gamma_{\mathrm{I}}^2 = \gamma_{\mathrm{I}}$, which is equivalent to idempotency of the N-normalized one-matrix. Note that any γ with at least one but less than N eigenvalues equal to $1/N$ covers a boundary point of $\mathcal{P}_N^1$.

Now due to the convexity of $\mathcal{P}_N^1$, any general member $\gamma(\mathbf{x},\mathbf{x}')$ can be represented by

$$\gamma(\mathbf{x},\mathbf{x}') = a\,\gamma_{\mathrm{I}1}(\mathbf{x},\mathbf{x}') + b\,\gamma_{\mathrm{I}2}(\mathbf{x},\mathbf{x}') + \cdots \tag{2.13}$$

and the convex set $\mathcal{P}_N^1$ is, therefore, the convex closure of the set of all γ_{I}.

It is well known that idempotent one-kernels correspond with N-particle wave functions of single Slater-determinant form

$$\gamma_{\mathrm{I}}(\mathbf{x},\mathbf{x}') = \frac{1}{N}[\phi_1(\mathbf{x})\phi_1^*(\mathbf{x}') + \cdots + \phi_N(\mathbf{x})\phi_N^*(\mathbf{x}')], \tag{2.14}$$

where the wave function is

$$\Phi_D = (N)^{-1/2}\det[\phi_1(\mathbf{x}_1)\phi_2(\mathbf{x}_2)\cdots\phi_N(\mathbf{x}_N)] \tag{2.15}$$

and "det" indicates the Slater determinant formed from the eigenvectors of γ_{I}. For such a system the two-matrix is a function of the one-matrix and hence the total energy is a function of the one-matrix alone. Examples of such wave functions are those in Hartree-Fock or in Kohn-Sham theory [39].

We now wish to consider some specific members of the set $\mathcal{P}_N^1$. Define an element of $\mathcal{P}_N^1$ as γ_{X}

$$\gamma_{\mathrm{X}}(\mathbf{x},\mathbf{x}')=\frac{1}{R}\sum_{k=1}^{R}\phi_k(\mathbf{x})\phi_k^*(\mathbf{x}'), \tag{2.16}$$

where R the rank of the one-kernel tends to infinity. The existence of γ_{X} as $R\rightarrow\infty$ can be proven using the Gilbert construction [40]. Now since all eigenvalues are degenerate at $1/R$, this one-kernel is unique since any unitary transformation amongst degenerate eigenvectors does not change the kernel. Now consider a general member γ_{V} of the set $\mathcal{P}_N^1$. Irrespective of the eigenvectors of γ_{V}, we can always rotate those of γ_{X} to coincide with them and hence both kernels are defined with the same eigenvectors. As was pointed out by Harriman [41], since both γ_{X} and γ_{V} have the same eigenvectors, the distance between γ_{X} and γ_{V} in the sense of a Euclidean vector space may be written in terms of the eigenvalues alone as

$$d_{\mathrm{XV}}=\left[\sum_{i=1}^{R}\left(\frac{1}{R}-n_i\right)^2\right]^{1/2}, \tag{2.17}$$

where n_i are the eigenvalues of γ_{V}.

Now consider another one-kernel, γ_{I} which has N eigenvalues of $1/N$ with all others being zero. This is an extreme element of $\mathcal{P}_{\mathrm{N}}^1$. γ_{X} can again be rotated to have coincidental eigenvalues with γ_{I} and the distance between these two elements is then

$$d_{\mathrm{XI}}=\left[\sum_{i=1}^{N}\left(\frac{1}{R}-\frac{1}{N}\right)^2+\sum_{i=N+1}^{R}\left(\frac{1}{R}\right)^2\right]^{1/2}=\left[\frac{(R-N)}{RN}\right]^{1/2} \tag{2.18}$$

and hence the extreme elements of $\mathcal{P}_N^1$ will lie on a hypersphere of radius $[(R-N)/RN]^{1/2}$ about γ_{X}.

The closest extreme element of $\mathcal{P}_N^1$ to γ_{V} is the member of γ_{I} with the same eigenvectors as γ_{V} and lies at a distance d_{VI} away, where

$$d_{\mathrm{VI}}=\left[\sum_{i=1}^{N}\left(\frac{1}{N}-n_i\right)^2+\sum_{i=N+1}^{R}n_i^2\right]^{1/2}. \tag{2.19}$$

This defines a unique distance measure from an arbitrary member of $\mathcal{P}_N^1$ to the closest extreme point, or in other words the distance that the arbitrary kernel is from representability by a Slater determinant. The corresponding member of γ_{I} is known as the ''best-density'' kernel defined by Kutzelnigg and Smith [42].

III. CONVEX AND CONCAVE FUNCTIONALS

In the preceding section, we introduced the idea that $\mathcal{P}_N^1$ is a convex set and also highlighted a unique distance measure. If we wish to study relationships between members of a convex set, it is pertinent to use convex functionals defined on the set [43–45]. In particular, we will be interested in the relations between a general member of a convex set and the limit points.

Let f be a real-valued function defined on a convex set D. f is convex if

$$f(ax+by)\leqslant af(x)+bf(y) \tag{3.1}$$

with $a+b=1$; $a,b\geqslant 0$. Conversely, a concave functional satisfies

$$f(ax+by)\geqslant af(x)+bf(y). \tag{3.2}$$

A concave functional f attains its minimum value at the extreme points of a convex set and has greater values at the interior points. A simple concave functional of interest was first defined by Löwdin [35]. Here, we write it in terms of one-normalized occupation numbers

$$C_L=\sum_i Nn_i(1-Nn_i)=N-N^2\sum_i n_i^2. \tag{3.3}$$

It was used as a measure of how dissimilar a wave function is to a Slater determinant. If the N-largest eigenvalues of the one-matrix are greater then $1/2N$ and the remaining $R-N$ eigenvalues are less than $1/2N$, which is almost certainly the case for Coulomb systems, C_L has a monotonic relationship with d_{VI} previously defined [Eq. (2.19)], in that it is zero for γ_{I} and increases as one moves to the interior of the set towards γ_{X}. Ziesche [46] calls this functional (with a prefactor of N^{-1}) the nonidempotency per particle. He also generalizes it to the νth order,

$$C_\nu=1-\frac{1}{N}\sum_i (Nn_i)^\nu=1-N^{\nu-1}\sum_i n_i^\nu. \tag{3.4}$$

Interestingly, the slope of C_ν at $\nu=1$ is

$$\left.\frac{dC_\nu}{d\nu}\right|_{\nu=1}=-\sum_i n_i\ln n_i-\sum_i n_i\ln N=S_J-\ln N. \tag{3.5}$$

N is constant for a fixed number of electrons, and $C_L=NC_2$ has a monotonic relationship with d_{VI}. Furthermore, all C_ν have a monotonic relationship among each other, and so has the slope Eq. (3.5), i.e., if one increases, so do all of them. It follows that there is a monotonic relationship between C_L and S_J and hence between d_{VI} and S_J. The functional S_J, the Jaynes entropy, is of great importance in the information theory as a measure of the information content of a probability distribution and hence is often referred to as ''information entropy'' [26,47,48].

We have, therefore, succeeded in making a connection between the topology of $\mathcal{P}_N^1$ and the information theory, in particular, it has been shown that the distance measure from an extremity in a Euclidean vector space d_{VI} monotonically increases with the so-called Jaynes information entropy of the one-matrix.

IV. ELECTRON CORRELATION AND COLLINS' CONJECTURES

In discussions of electron correlation, the traditional quantum-chemical definition of the uncorrelated reference system has been the Hartree-Fock wave function Ψ_{HF}. The correlation energy is defined as the difference between the exact, nonrelativistic ground-state energy and the exact Hartree-Fock energy [49]

$$E_c = E_o - E_{HF} \leqslant 0. \tag{4.1}$$

It was conjectured by Collins [29] that the Jaynes entropy of the N-normalized one-matrix S_J^N [50] is directly proportional to the negative of the correlation energy of the system

$$-E_c = -\chi \sum_i n_i \ln n_i = S_J^N \chi, \tag{4.2}$$

where χ is a positive constant, a hypothesis that has some supporting numerical evidence [51] and some modifications to it have been considered [52]. A second conjecture of Collins was that maximization of the entropy subject to the constraint of fixed density produces the correct one-matrix.

To deal with the first conjecture, we note that the entropy is a function of the one-matrix, while the standard correlation energy is a function of the full, many-body wave function, Ψ_o for a pure state, or Γ for an ensemble. In this work we use a definition of the correlation energy that is provided by the density-functional theory, and which uses a more well-defined independent variable, namely, the coupling constant λ.

Consider the partly coupled Schrödinger equation

$$[\hat{T} + v_{ext}(\mathbf{r}) + v_{eff}^{\lambda}(\mathbf{r}) + \lambda \hat{V}_{ee}]\Psi^{\lambda} = E\Psi^{\lambda}, \tag{4.3}$$

where the coupling constant $\lambda \in [0,1]$, $v_{ext}(\mathbf{r})$ is the external potential arising from the nuclei in a molecule, $\hat{T}$ is the standard kinetic-energy operator and $\hat{V}_{ee}$ is the electron-electron interaction operator. The local effective potential $v_{eff}^{\lambda}(\mathbf{r})$ is chosen such that the true ground-state density $\rho_o(\mathbf{r})$ is obtained for all λ. The task of finding Ψ^{λ} in Eq. (4.3) can be replaced by a constrained search over all $\Psi \mapsto \rho_o(\mathbf{r})$ [53]

$$\min_{\Psi \mapsto \rho_o} \langle \Psi | \hat{T} + \lambda \hat{V}_{ee} | \Psi \rangle. \tag{4.4}$$

For the $\lambda = 0$ case, this becomes the search for the noninteracting kinetic energy

$$T_s[\rho_o] = \min_{\Psi \mapsto \rho_o} \langle \Psi | \hat{T} | \Psi \rangle, \tag{4.5}$$

where $\Psi^{\lambda=0}$ is now a unique single determinant assuming nondegeneracy of the noninteracting system. It is clear that we can rewrite this in terms of a search over the convex set of N-representable one-matrices, which have $\rho_o(\mathbf{r})$ as their diagonal,

$$\frac{1}{N} T_s[\rho_o] = \min_{\gamma \rightarrow \rho_o} \mathrm{tr}[\hat{T}\gamma(\mathbf{x},\mathbf{x}')] \tag{4.6}$$

and since it is the optimization of a linear functional on a convex set, the minimium occurs at an extreme point of the set, which is the idempotent one-matrix in correspondence with the determinant obtained in Eq. (4.5). The optimization in Eq. (4.6) cannot be applied to $\lambda > 0$ since λV_{ee} is no longer a function of the one-matrix. We can, however, perform a similar constrained search over the convex set of N-representable two-matrices

$$\min_{\Gamma \mapsto \rho_o} \mathrm{tr}[(\hat{H}^1 + \lambda \hat{H}^2)\Gamma(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2)]. \tag{4.7}$$

Note that the N-representability conditions on the two-matrix are not known in a tractable form. This optimization results in a two-matrix, which reduces under the action of $\mathcal{L}_2^1$ to a nonextreme one-matrix.

A useful definition of the correlation energy from the density-functional theory is just the difference between the total energies of the fully interacting and noninteracting systems, yielding the true density

$$E_c[\rho_o] = \mathrm{tr}[\hat{K}(\Gamma^{\lambda=1}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2) - \Gamma^{\lambda=0}(\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1',\mathbf{x}_2))], \tag{4.8}$$

which has been rewritten by Savin [27] and Levy and Görling [28] as an integral along an adiabatic connection [54,55] linking the noninteracting and fully interacting one-matrices

$$E_c[\rho_o] = -\int_0^{\lambda=1} \frac{T[\gamma^{\lambda}] - T_s[\rho_0]}{\lambda^2} d\lambda. \tag{4.9}$$

The partially interacting density matrix γ^{λ} in this equation is the one obtained from Ψ^{λ} of Eq. (4.3) by reduction [Eq. (2.3)]. This equation also serves to define a λ-dependent correlation energy E_c^{λ} by replacing $\lambda = 1$ in the upper integration limit by an arbitrary value. The integrand is positive since the kinetic energy of a partly interacting system is always greater than that of a noninteracting system [56].

We now wish to consider the behavior of the eigenvalue spectrum of γ^{λ}. $\gamma^{\lambda=0} \in \{\gamma_{\mathrm{I}}\}$ and is, therefore, extreme in $\mathcal{P}_N^1$. The entropy is, therefore, at a minimum but as λ is increased, those eigenvalues formerly at $1/N$ become smaller while the remainder becomes larger and hence S_J increases. We do not know the value of S_J^{λ} for each λ but in the light of the "geometric" considerations of the preceding two sections, it is reasonable to assume that it is a monotonically increasing function of λ [57]. If this is true, we may use S_J as the integration variable in the coupling constant integration by making λ a monotonically increasing function of S_J

$$E_c[\rho_o] = -\int_0^{S_J(\lambda=1)} \frac{T[\gamma^{S_J}] - T_s[\rho_0]}{\lambda^2(S_J)} \left(\frac{d\lambda(S_J)}{dS_J}\right) dS_J. \tag{4.10}$$

Note that the Jacobian $d\lambda(S)/dS_J$ is positive due to the monotonicity of the $\lambda \leftarrow S_J$ mapping. Clearly, the derivative of this expression at $\lambda(S_J) = 1$ is negative,

$$-\left.\frac{dE_c}{dS_J}\right|_{\lambda=1} = [T - T_s]\left.\frac{d\lambda}{dS_J}\right|_{\lambda=1} > 0 \tag{4.11}$$

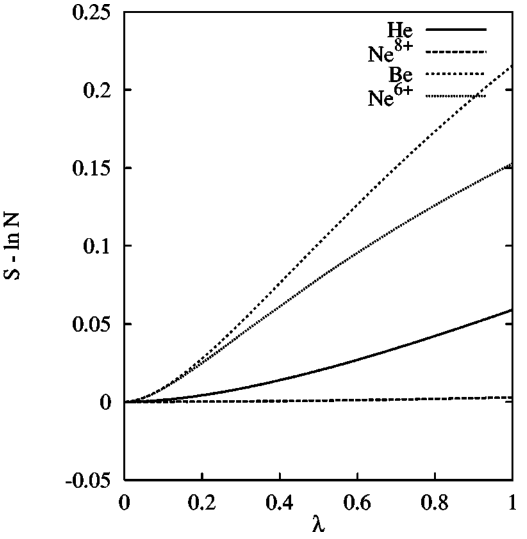

FIG. 1. Entropy S_J as a function of the coupling constant λ for a few two- and four-electron systems [58].

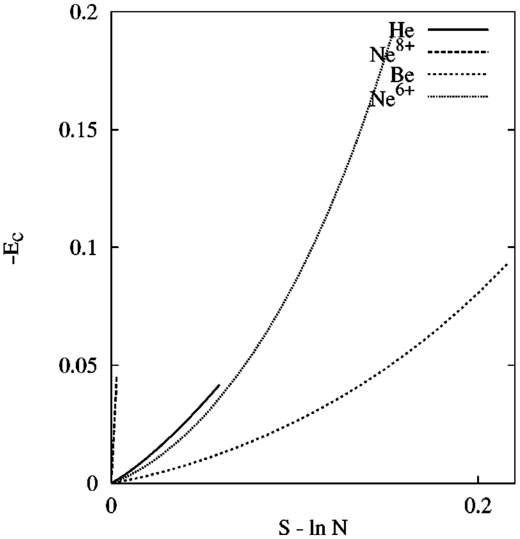

FIG. 2. Correlation energy E_c^λ [see Eq. (4.9)] versus entropy S_J^λ [58].

so that we have proven the following theorem: *If* S_J *is a monotonically increasing function of* λ, *then there is a montonically decreasing relationship between the information entropy and the correlation energy* in the fully interacting system.

Since the premise in this theorem is plausible but not proven, this leads to our "modified Collins' conjecture": As the correlation energy E_c, in its density-functional theory definition, *decreases* (i.e., becomes more negative), the information entropy S_J increases. This is, of course, weaker than the original conjecture, but it is physically plausible. Ziesche *et al.* have empirically arrived at a very similar modification of Collins' conjecture on the grounds of their analysis of two-particle systems [52].

Colonna and Savin have recently produced Ψ^λ along the adiabatic connection for a number of two- and four-electron systems [58]. Using their results for He, Be, Ne^{6+}, and Ne^{8+}, we have calculated S_J^λ and Fig. 1 confirms the monotonic relationship of S_J^λ with λ for these atoms and ions. Of greater interest is the relationship of $E_c[\rho_o]$ with S_J^λ as shown in Fig. 2 for the same systems. Again there is a monotonicity of the two quantities confirming our modified Collins' conjecture, but a simple proportionality is absent.

The second conjecture of Collins was that the true one-matrix is obtained by applying the maximum-entropy principle of Jaynes [59] subject to the constraint of fixed density. We know that a one-matrix with any eigenvalue structure can describe any density [60] and hence a γ with a flat eigenvalue spectrum would result. This is certainly not the correct one-matrix, since its kinetic energy is far too great. The maximum-entropy principle states that one should satisfy all known constraints and then maximize the entropy. We conjecture that the additional constraint of fixed kinetic energy will produce a one-matrix with the correct entropy. This suggests a methodology for the direct determination of the true one-matrix of the system from its density and its kinetic energy: Of the set of *N*-representable one-particle density matrices $\gamma(\mathbf{x},\mathbf{x}')$, which collapse to the true ground-state density $\rho_o(\mathbf{r})$ and *that yield the true value of the kinetic energy*, the one maximizing the information entropy is uniquely defined and is the true one-matrix. This then defines a new constrained search-type definition for the one-matrix

$$S_J = \max_{\gamma\to\rho_o,T}\left(-\sum_i n_i[\gamma]\ln n_i[\gamma]\right). \qquad (4.12)$$

This scheme would apply for arbitrary values of the coupling constant since this information is already supplied by T^λ. At $\lambda=0$, the kinetic energy $T=T_s$ is at its minimum value and we know this can only occur at the extreme points of the convex set and hence the eigenvalue spectrum is completely fixed. The set $\{\gamma\mapsto\rho_o,T_s\}$ reduces to a single member and there is no space over which to maximize the entropy. However, as T^λ increases, a set of one-matrices, all degenerate in the one-electron energy E^1, results. For each value of the coupling constant, the actual γ^λ is the one which is the contraction of Γ^λ under the action of $\mathcal{L}_2^1$, however, at the level of the one-matrix alone, we cannot identify it without recourse to something other than $\hat{H}^1$, and we conjecture that maximization of the entropy picks out the true γ^λ. If this is indeed the case, it provides an additional argument that the entropy always increases as $\lambda:0\mapsto1$, since T^λ is a monotonic increasing function of λ and we are moving from the hull of the convex set towards its interior, the maximum attainable value of the entropy must increase.

It should be noted that there is no explicit information in either the density, the kinetic energy, or the entropy about the nature of the electron-electron interaction. How can we expect to derive from these quantities the true one-matrix, which is, after all, a reduced form of the exact wave function? A possible answer might be that the relationship is *implicit*, i.e., a specific combination of density and kinetic energy is physically only possible if the electron-electron interaction has a specific (namely, the Coulomb) form.

If the true density is known (e.g., from x-ray diffraction), and so is the kinetic energy (e.g., from Compton scattering), then this would be a practical way of going about determining the density matrix from experimental data, which is a problem of long standing indeed (see [61–63] and references therein).

V. CONCLUDING REMARKS

We have made an argument that Collins' conjecture about the relationship of the one-particle information entropy of a system and its correlation energy can be formulated in a modified manner, leading to a *monotonic* relationship between the *density-functional* definition of the correlation energy and the information entropy of the system. This differs from the original formulation [29] that postulated a *proportionality* between the information entropy and the *standard* definition of the correlation energy (i.e., the difference between the total energy and the Hartree-Fock energy of the system).

This reformulation was deemed necessary since the absence of a simple proportionality can be demonstrated empirically [51,52]. Furthermore, the original Collins' conjecture does not make any statements about the independent variable on which both the correlation energy and the information entropy depend. In this work, we have identified this variable with the coupling constant λ. Finally, there is no known *explicit* expression linking the standard definition of the correlation energy to a one-particle quantity. This suggests the use of the density-functional theory definition, since for the latter, such an expression exists in Eq. (4.9).

We further suggest that the maximum-entropy principle be used for the construction of the one-particle reduced density matrix from experimentally known densities and kinetic energies. This is in contrast to Collins' suggestion to focus exclusively on the density. We would like to point out that it has been shown by Harriman [64], that both in the actual case, and within a finite basis set of "reasonable" size, the unique determination of the one-matrix from charge densities in *both* position *and* momentum space is impossible. Perhaps the maximization of information entropy supplies the missing piece to make this determination unique. We hope this contributes one more step towards an understanding of the feasibility of direct density matrix reconstruction, and of the conditions that have to be met.

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