

Information entropy as a measure of the correlation energy associated with the cumulant

Yu Wang,¹ P. J. Knowles,² and Jian Wang^{3,*}

¹*Department of Physics, Jiaying University, Zhejiang 314001, China*

²*School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff CF10 3AT, United Kingdom*

³*School of Science, Huzhou University, Zhejiang 313000, China*



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A linear relation is found between Jaynes entropy and the correlation energy associated with the cumulant for a correlated molecular system, as demonstrated in H₂ and a water molecule. The relation modifies the Collins conjecture, in which the correlation energy is defined as the total energy difference with reference to the Hartree-Fock counterpart. The linear behavior is system dependent and shifts slightly on a different basis set. This correlation energy is extensive. For a system whose wave function can be expressed as the antisymmetrized product of orthogonal groups, the correlation energy is just the sum of the individual groups. The finding offers a convenient way to construct an approximate correlation energy functional in reduced density-matrix-functional theory, which may be used in large-scale molecular dynamics simulations and potential energy surface calculations where the molecular geometry needs to be frequently updated.

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I. INTRODUCTION

The reduced density-matrix-functional theory (RDMFT) is an extension of the density-functional theory (DFT) [1]. The fundamental variable in RDMFT is the one-particle density matrix (1-matrix for short), which has an eigenfunction expansion

$$\gamma(1, 1') = \sum_i n_i \chi_i(1) \chi_i^*(1'), \quad (1)$$

where the eigenfunctions $\chi_i(1)$ are called the natural orbitals. The eigenvalues n_i are their occupation numbers, which have the property $\sum n_i = N$.

The advantage of RDMFT is that the kinetic energy is explicitly defined in terms of the 1-matrix and hence does not require the construction of an approximate functional, so only the two-electron Coulomb repulsion energy need to be modeled as a functional of the 1-matrix. The two-electron repulsion energy is usually expressed as

$$U_{ee} = \int \frac{\Gamma(1, 2)}{r_{12}} d1d2 = \sum_{ijkl} \Gamma_{ij,kl} \langle ij|kl \rangle, \quad (2)$$

where $\Gamma(1, 2)$ is the diagonal elements of the two-particle density matrix (2-matrix), also called the pair density. $\langle ij|kl \rangle$ are the two-electron integrals. In the method of the configuration interaction (CI), $\Gamma_{ij,kl}$ depend on the expansion coefficients of the wave function. In RDMFT, $\Gamma_{ij,kl}$ are regarded as functionals of 1-matrix γ in principle. However, since the orbitals are already contained in the two-electron integrals $\langle ij|kl \rangle$, one usually assumes $\Gamma_{ij,kl}$ as only functionals of the occupation numbers n_i . In practical functionals, the functionals of $\Gamma_{ij,kl}$

often take the square-root form $\sqrt{n_i}$ [2–10], or the power-law form [11] n_i^α , with $\alpha \approx 0.656$.

The cumulant of a 2-matrix is defined as [12,13]

$$\lambda(1, 2) = \Gamma(1, 2) - \frac{1}{2}[\gamma(1, 1)\gamma(2, 2) - \gamma(1, 2)\gamma(2, 1)], \quad (3)$$

where γ is the 1-matrix originating from the same wave function as $\Gamma(1, 2)$. While the 2-matrix is a product-separable quantity as the wave function, it is not extensive. The cumulant has the nice property of being an extensive, additively separable entity [12]. $\gamma(1, 1)\gamma(2, 2)$ is the pair density of independent particles, while $\gamma(1, 2)\gamma(2, 1)$ is the exchange effect. The cumulant $\lambda(1, 2)$ contains the effect of the Coulomb correlation.

In DFT and also in RDMFT, the effects of exchange and Coulomb correlations were often modeled together through the exchange-correlation hole [3,14–17], which is responsible for the exchange-correlation energy. Another strategy is to treat the exchange and Coulomb correlation separately, where the two-electron repulsion energy associated with the cumulant is regarded as the correlation energy [12,18],

$$E_{\text{cum}} = \int \frac{\lambda(1, 2)}{r_{12}} d1d2. \quad (4)$$

The exchange effect can be either treated in the sense of a Hartree-Fock approximation or treated in $\gamma(1, 2)\gamma(2, 1)$, with γ originated from the correlated system. In quantum chemistry, there is another definition of correlation energy, which is defined as the total energy beyond the Hartree-Fock (HF) energy [19],

$$E_{\text{corr}} = E - E_{\text{HF}}. \quad (5)$$

*jwang572@hotmail.com

TABLE I. The entropy S and the two-electron energies (in a.u.) of H_2 as a function of nuclear distance R (in bohrs) calculated with the basis set aug-cc-pV6Z(s). U_{ee} and U_{0ee} are the two-electron energies in CI and HF. Y is the two-electron energy calculated with the K matrix defined in Eq. (6). The last column is calculated with the equation $y = \kappa S + b$, with $\kappa = 0.20493$ and $b = 0.02808$. Note that the first line with a value $R = 0$ corresponds to He.

R	S	U_{ee}	U_{0ee}	Y	$U_{0ee} - U_{ee}$	$Y - U_{ee}$	$\kappa S + b$
0 (He)	0.057310	0.986680	1.025765	1.026550	0.039085	0.039870	0.039824
1	0.124041	0.694978	0.740185	0.749924	0.045207	0.054946	0.053499
1.5	0.192451	0.583512	0.632665	0.650976	0.049153	0.067464	0.067519
2	0.311832	0.495968	0.554921	0.587658	0.058953	0.091689	0.091983
2.5	0.492541	0.423017	0.497354	0.551602	0.074337	0.128585	0.129017
3	0.721646	0.360038	0.453749	0.535385	0.093711	0.175347	0.175967
3.25	0.841128	0.332003	0.435953	0.531821	0.103950	0.199818	0.200452
3.5	0.954344	0.306404	0.420320	0.529496	0.113915	0.223092	0.223654
4	1.139767	0.262911	0.394383	0.524302	0.131472	0.261391	0.261652
4.5	1.258862	0.229245	0.374154	0.515317	0.144910	0.286072	0.286059
5	1.324434	0.203516	0.358408	0.503182	0.154893	0.299666	0.299496
6	1.373014	0.167443	0.336622	0.477180	0.169179	0.309737	0.309452
7	1.383598	0.143015	0.323178	0.454952	0.180163	0.311937	0.311621
8	1.385763	0.125031	0.314503	0.437420	0.189472	0.312389	0.312065
10	1.386275	0.100001	0.303941	0.412497	0.203941	0.312495	0.312169

The Hartree-Fock energy is the minimum for any 2-matrix of the form [20]

$$K(1, 2) = \frac{1}{2}[\gamma(1, 1)\gamma(2, 2) - \gamma(1, 2)\gamma(2, 1)]. \quad (6)$$

This form is exact in the Hartree-Fock method [21], i.e., the cumulant is zero in Hartree-Fock.

Information entropy [22] is a measure of available information, complete or incomplete, given a set of possible events with probabilities p_1, p_2, \dots, p_n , where $\sum_i p_i = 1$. On the other hand, the probability distribution can be regarded as the result of a maximum-entropy principle subject to certain constraints [23]. For example, the Gaussian distribution is the result of maximum entropy subject to the condition that the standard deviation be fixed at σ . The square of the absolute value of the wave function has a physical interpretation as a probability distribution. Information entropies based on density matrices or density have been the topic of extensive investigations for many years [24–29].

For the information entropy on the 1-matrix, Jaynes [30] has given the form

$$S = - \sum_i n_i \ln n_i. \quad (7)$$

For the Hartree-Fock approximation, since n_i are either 0 or 1, the entropy is zero. In the CI method, $0 < n_i < 1$, the entropy is positive. As the correlation energy, the entropy can be regarded as a measure of correlation strength.

Collins [31] once conjectured that the correlation energy, E_{corr} with the sign reversed, be proportional to Jaynes entropy,

$$E_{\text{corr}} = \kappa \sum_i n_i \ln n_i, \quad (8)$$

where κ is a constant. Numerical evidence for the conjecture has since been reported in the lithium isoelectronic series and small molecules using sequences of increasingly large basis sets [32,33], while discrepancies have also been found [34,35].

The design of a RDMFT functional often faces the choice as to which 2-matrix elements to model. Most RDMFT functionals are two-index JK type, i.e., containing only $J_{ij} = (ii|jj)$ and $K_{ij} = (ij|ji)$ spatial two-electron integrals [36]. Such functionals can be easily regarded as incomplete in representing the 2-matrix of real molecules from the wave function, because many of the matrix elements with different i, j, k, l indices are neglected. Given the fact that our knowledge of the 2-matrix or cumulant of a real molecule is limited, what is the best guess for a RDMFT functional? The motivation of this article is to find a method which can cover all the information in the 2-matrix, maybe of a statistical nature, so we land on the concept of information entropy.

II. COMPUTATION RESULTS

Figure 1 displays the entropy S as a function of internuclear distance R (in bohrs) in H_2 . The data are listed in Table I,

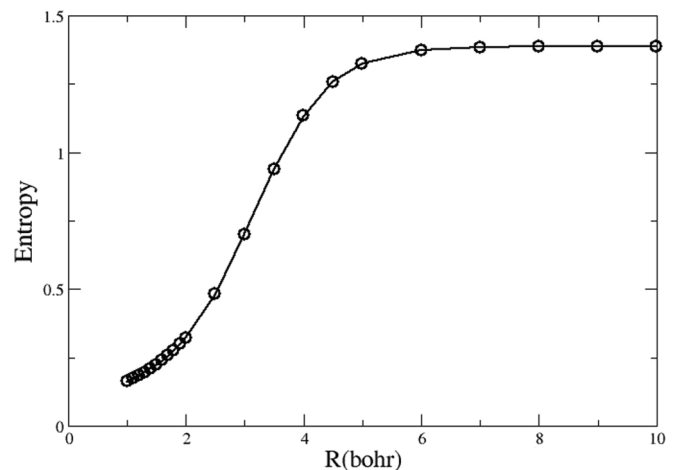


FIG. 1. Jaynes entropy of H_2 is given as a function of internuclear separation R .

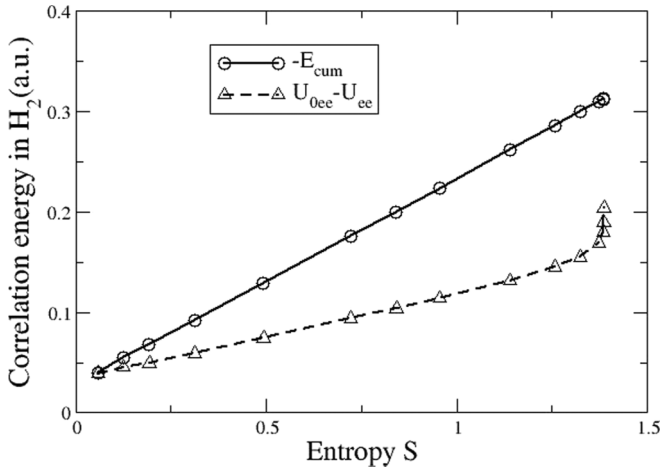


FIG. 2. The correlation energy associated with the cumulant as a function of Jaynes entropy in H_2 . Also in display are the differences of two-electron energy between the HF and CI calculations, $U_{0ee} - U_{ee}$.

which also contains other essential data for our analysis. U_{ee} and U_{0ee} are the two-electron repulsion energies in CI and HF calculations. Y is the two-electron energy calculated with the K matrix defined in Eq. (6),

$$Y = \int \frac{K(1, 2)}{r_{12}} d1d2, \quad (9)$$

where the 1-matrix is from the correlated CI wave function. The data were calculated with the MOLPRO code [37] using the augmented correlation-consistent polarized valence sextuple zeta basis set [aug-cc-pV6Z(s)], which gives a total energy -1.15485 a.u. at an equilibrium bond length $R = 1.4$ bohrs. The first line in Table I with a bond length $R = 0$ corresponds to the He atom. The entropy for the He atom is small, which means the Hartree-Fock approximation is a good approximation.

From Eqs. (2)–(4) and (9), the correlation energy associated with the cumulant can be written as

$$E_{cum} = U_{ee} - Y. \quad (10)$$

In Fig. 2, $-E_{cum}$ (with a sign change) is plotted as a function of entropy. The data fall on almost a straight line with the equation $y = 0.20493x + 0.02808$. For comparison, we also display the energy difference of $U_{0ee} - U_{ee}$ as a function of the entropy. Note that U_{0ee} is closer to U_{ee} than Y , because their difference is smaller. However, the linear behavior of $U_{0ee} - U_{ee}$ with S is limited to a nuclear distance $R < 4$ bohrs.

In the original conjecture of Collins, the correlation energy is referred to as the energy difference with respect to the Hartree-Fock reference. The correlation energy associated with the cumulant has no reference to the Hartree-Fock. Both the correlation energy associated with the cumulant and the entropy come from the same CI wave function, so one may expect a closer relationship between them.

Figure 3 compares the data from two basis sets. The data from the correlation-consistent polarized valence double zeta (cc-pVDZ) basis set can be represented by the line $y = 0.19886x + 0.03687$ after linear regression. The figure

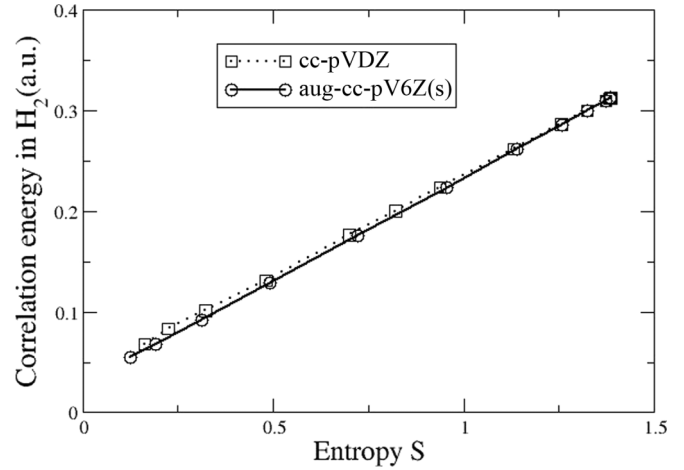


FIG. 3. The comparison of a linear relation between the correlation energy associated with the cumulant and entropy for two basis sets in H_2 , aug-cc-pV6Z(s) and cc-pVDZ.

indicates that the linear behavior shifts only slightly with a different basis set.

Next, we study the water molecule H_2O , which has three internal coordinates: two H-O bond lengths R_1 and R_2 , plus the angle θ between them. Table II lists the entropies and the two-electron energies at selected geometries. The data are calculated in the complete active space self-consistent field method (CASSCF) with six electrons in 14 active orbitals. The wave function consists of 41 405 configuration state functions with the cc-pVDZ basis set [38,39]. At short bond lengths, such as $R_1 = R_2 = 1.5$ bohrs, the wave function is dominated by a single determinant. As the bond length increases, the wave function evolves into a multiconfiguration character.

A linear relation between the correlation energy $-E_{cum}$ and the entropy is suggested in Fig. 4. The data fit well to a line $y = 0.220x + 0.188$. On the other hand, although U_{ee} is closer

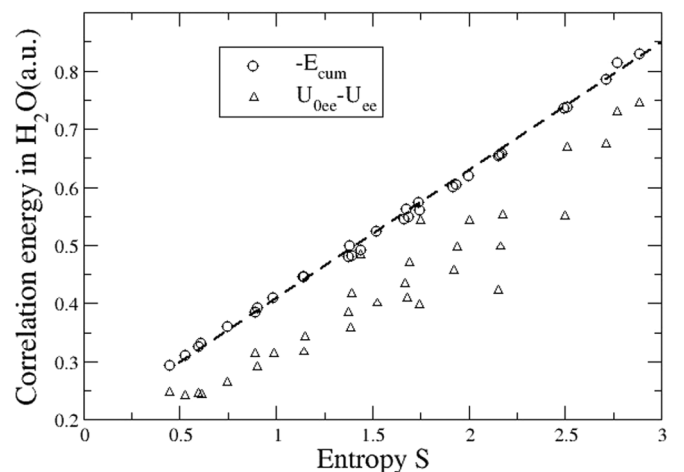


FIG. 4. The correlation energy associated with the cumulant is plotted with respect to Jaynes entropy in H_2O . For comparison, the differences of two-electron energies between HF and CI calculations, $U_{0ee} - U_{ee}$, are also in display. The data are from Table II.

TABLE II. The entropy and the two-electron energies (in a.u.) of H₂O in different geometries. U_{ee} and U_{0ee} are the two-electron energies in CI and HF, respectively, and Y is the two-electron energy calculated with the K matrix defined in Eq. (6). The last column is calculated with the equation $y = \kappa S + b$ with $\kappa = 0.220$ and $b = 0.188$. R_1 and R_2 are the two H-O bond lengths in bohrs. θ is the angle between R_1 and R_2 in degrees.

R_1	R_2	θ	S	U_{ee}	U_{0ee}	Y	$U_{0ee} - U_{ee}$	$Y - U_{ee}$	$\kappa S + b$
1.5	1.5	104	0.447087	39.064798	39.312136	39.357279	0.247338	0.292481	0.286359
1.8	1.8	104	0.526674	37.722447	37.963486	38.033270	0.241039	0.310823	0.303868
2	2	104	0.595617	36.986606	37.231660	37.313227	0.245054	0.326621	0.319036
2	2	90	0.609942	36.967875	37.212002	37.299243	0.244127	0.331368	0.322187
2	2.5	104	0.745890	36.236543	36.500731	36.595816	0.264189	0.359273	0.352096
1.5	3	104	0.889759	36.662127	36.976472	37.047850	0.314345	0.385724	0.383747
2.5	2.5	104	0.900551	35.486458	35.777764	35.879857	0.291306	0.393399	0.386121
2	3	104	0.986128	35.626489	35.940774	36.036289	0.314286	0.409800	0.404948
2.5	3	90	1.141746	34.880323	35.197098	35.326184	0.316775	0.445860	0.439184
2.5	3	104	1.148155	34.885203	35.227302	35.331534	0.342099	0.446331	0.440594
3	3	90	1.374675	34.282773	34.667292	34.763037	0.384519	0.480264	0.490429
3	3	80	1.382758	34.305482	34.662602	34.803919	0.357121	0.498437	0.492207
3	3	104	1.390706	34.276027	34.692169	34.758889	0.416142	0.482863	0.493955
3	3	120	1.438320	34.263161	34.746261	34.755164	0.483100	0.492003	0.504430
2	4	104	1.521517	34.755153	35.155770	35.279608	0.400618	0.524455	0.522734
3	3.5	90	1.667492	33.819201	34.252549	34.363982	0.433348	0.544781	0.554848
3	3.5	80	1.678650	33.837549	34.246983	34.400346	0.409433	0.562797	0.557303
3	3.5	104	1.689364	33.804977	34.275344	34.353956	0.470367	0.548979	0.559660
2	5	104	1.741337	34.277427	34.675835	34.850119	0.398408	0.572692	0.571094
3	3.5	120	1.747984	33.781337	34.323986	34.342397	0.542649	0.561060	0.572557
3	4	90	1.919319	33.465431	33.921772	34.066499	0.456341	0.601068	0.610250
3	4	104	1.938484	33.448845	33.945942	34.053805	0.497097	0.604960	0.614467
3.5	3.5	104	2.001886	33.331423	33.874856	33.950577	0.543432	0.619154	0.628415
3	5	80	2.154470	33.006174	33.428903	33.659715	0.422729	0.653541	0.661984
3	5	104	2.161299	32.980526	33.478324	33.635364	0.497799	0.654838	0.663486
3	5	120	2.174584	32.967727	33.519918	33.625557	0.552191	0.657830	0.666409
4	4	80	2.497713	32.639433	33.189503	33.374162	0.550069	0.734728	0.737497
4	4	104	2.509576	32.608406	33.276648	33.345219	0.668242	0.736814	0.740107
4	5	90	2.712706	32.156415	32.830529	32.942097	0.674114	0.785682	0.784795
4	4.5	104	2.770996	32.295342	33.024311	33.108991	0.728970	0.813650	0.797619
5	5	104	2.884660	31.684340	32.428983	32.512980	0.744642	0.828640	0.822625

to U_{0ee} than Y in magnitude, the difference of $U_{0ee} - U_{ee}$ is much scattered with respect to the entropy.

The above results suggest an approximation of the correlation energy associated with the cumulant in terms of the entropy,

$$E_{\text{cum}} = \kappa \sum_i n_i \ln n_i - b, \quad (11)$$

where κ and b are positive constants depending on the system and the basis set, but insensitive to the geometry. Once they are calculated, one can use them as known parameters, or one may find them on the spot by two independent CI calculations to find two points on the line. The formula is thus convenient for the molecular dynamics simulation and potential energy surface calculation [40] where the geometry needs to be frequently updated.

III. DISCUSSION AND CONCLUSION

Using the fact that the correlation energy associated with the cumulant is extensive, one may find some property of the constants κ and b . For example, for a system of two H₂ located

at a far distance, the combined system will have the same κ but b doubled. In general, for a wave function that can be approximated as the antisymmetrized product of orthogonal groups [41], the 2-matrix $\Gamma(1, 2)$ can be split into two parts: One part with the two electrons (1 and 2) in the same group, and another part with two electrons in different groups, say, the group I and J . The contribution to $\Gamma(1, 2)$ of the latter has the structure

$$\begin{aligned} \Gamma_{IJ}(1, 2) &= \gamma^I(1, 1)\gamma^J(2, 2) - \gamma^I(1, 2)\gamma^J(2, 1) \\ &\quad - \gamma^I(2, 1)\gamma^J(1, 2) + \gamma^I(2, 2)\gamma^J(1, 1). \end{aligned} \quad (12)$$

Such 1-matrix related terms have been included in the K matrix in Eq. (6), and they do not contribute to the correlation energy associated with the cumulant. So the correlation energy for the orthogonal groups is just the sum of the individual groups,

$$E_{\text{cum}} = \sum_I \kappa_I \sum_i n_i^I \ln n_i^I - \sum_I b_I, \quad (13)$$

where κ_I , n_i^I , and b_I are the data of the individual group I . In terms of correlation energy, orthogonal groups are just

isolated fragments. If correlation beyond exchange comes into play when we bring chemical groups together, then new parameters κ and b need to be established.

One example of orthogonal groups is the antisymmetrized product of strongly orthogonal geminals (APSG) [12,42], and its wave function is expressed as

$$\Psi(1, \dots, 2n) = A \prod_{m=1}^n \psi_m(2m-1, 2m), \quad (14)$$

where A is the usual antisymmetrizer. While there is exchange between different geminals, correlation exists only within the individual geminal.

In the multiconfiguration self-consistent field (MCSCF) or CASSCF method, the wave function for the whole system is the product of a determinant for the closed shells and a CI form for the active space. The orbitals in the closed shells may contribute a cross term to the 2-matrix $\Gamma(1, 2)$ in the form of Eq. (12) [43], but they do not contribute to the correlation energy. Only the orbitals in the active space contribute to the correlation energy and entropy.

A close analog to our finding is the electron gas in the Thomas-Fermi approximation. From Gell-Mann and Brueckner's work on the correlation energy of an electron gas at high density [44], Grassi *et al.* [45] obtained the following relation between the correlation energy per unit volume and Shannon entropy of the electron density,

$$E_c^{\text{egas}} = q_0 \int n(\mathbf{r}) \ln[n(\mathbf{r})] d\mathbf{r} - q_1 \int n(\mathbf{r}) d\mathbf{r}, \quad (15)$$

where $q_0 = 0.02073$ and $q_1 = 0.00584$ in a.u. The parameters q_0 and q_1 are similar to our parameters κ and b .

As Levy [18] noted, only a small piece of the exact universal variational functional of the 1-matrix is unknown, which is the correlation energy associated with the cumulant. Our result of Eq. (11) implies a simple functional of RDMFT for a correlated molecular system,

$$E = \sum_i n_i h_{ii} + \frac{1}{2} \sum_{i,j} n_i n_j \langle ij || ij \rangle + \kappa \sum_i n_i \ln n_i - b. \quad (16)$$

The functional contains only JK -type two-electron integrals as in the Hartree-Fock approximation. The contributions of other two-electron integrals are magically condensed into the entropy and the two parameters κ and b . In traditional 1-matrix functionals [46,47], one often introduces complicated phase structures to resolve the phase dilemma for the 2-matrix element $\Gamma_{ij,kl}$ [48,49]. There is no need to worry about the phases here, since all the different choices or uncertainties related to the phases and the matrix elements $\Gamma_{ij,kl}$ are treated statistically in the sense of information theory based on the premise of the maximum-entropy principle. Another problem with traditional 1-matrix functionals is their nonuniqueness, which means they cannot differentiate systems with the same 1-matrix eigenvalue spectrum but a different 2-matrix, because $\Gamma_{ij,kl}$ are usually treated as the functional of the occupation numbers only [50–52]. Due to the system-dependent parameters κ and b , the nonuniqueness problem can be relieved.

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