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Geminal-based statistics for the energies of many-electron molecular systems

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In 1959, Bopp developed a lower bound to atomic and molecular ground-state energies by summing the lowest eigenvalues of the two-particle reduced Hamiltonian, ${}^2\hat{K}$. His approximation is accurate only for very small systems (fewer than about four electrons), with the results degenerating rapidly for larger problems. In this paper, we extend and improve Bopp's work by introducing a flexible distribution function, guided by familiar Fermi-Dirac statistics, in order to generate occupation numbers for the energy levels of ${}^2\hat{K}$. The distribution function and the resulting energy are parametrized by a correlation temperature T. For a given system, characteristic temperatures may be identified that yield the true energy or any other benchmark energy of the system. Using a geometric argument and the empirical properties of the energy vs temperature curve, the two-electron statistics are investigated as a predictive tool for a variety of small atoms and molecules.

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I. INTRODUCTION

Around the middle of the 20th century, quantum chemists and physicists first considered using the two-electron reduced density matrix (2RDM) as the fundamental variable in quantum-chemical calculations [1–3]. Nearly 50 years later, the state of the art in RDM mechanics may be divided into two categories: (i) the solution of the anti-Hermitian contracted Schrödinger equation (ACSE) by cumulant reconstruction of the 3RDM from the 2RDM [4–7] and (ii) constrained variational minimization of the 2RDM, made possible by advances in semidefinite programming [8–13]. Both methods are mathematically rigorous and capable of calculating accurate ground-state energies of atoms and molecules.

However, before the development of these advanced methods, Bopp presented a conceptually simple means for understanding how two-body interactions can produce energies for N-particle systems [14]. In this work, we follow up Bopp's simple premise with an investigation into a different statistical approach to relating electron-pair energies to the energies of many-particle molecular systems. We believe that a better understanding of these statistics will enhance the possibility of developing electronic structure methods that, while not as rigorous as the ACSE and variational 2RDM methods [15], treat the electronic correlation problem more systematically than density functional theory (DFT). For this reason, the present work is in line with previous one- and two-electron functional theories, including natural-orbital functional theory [16–18].

A primary goal of electronic structure theory is determining ground-state energies from a system's N-body Hamiltonian and wave function,

$$E = \int \Psi^*(\mathbf{1},\mathbf{2},\ldots,\mathbf{N})\hat{H}\Psi(\mathbf{1},\mathbf{2},\ldots,\mathbf{N})d\mathbf{1}\cdots d\mathbf{N}, \qquad (1)$$

where each boldface integer represents the spin and spatial coordinates of that electron. Since atomic and molecular Hamiltonians contain only one- and two-body interactions and the electrons themselves are indistinguishable, it is possible to rewrite the N-body Hamiltonian in reduced form as

$${}^2\hat{K} = N\left(\hat{h}_1 + \frac{N-1}{2}\hat{V}_{12}\right). \qquad (2)$$

The operator ${}^2\hat{K}$, known as the *two-particle reduced Hamiltonian*, expresses the energy as the sum of N one-body terms, representing the kinetic and nuclear potential energies of each electron, and $\binom{N}{2}=\frac{N(N-1)}{2}$ two-body terms, representing the Coulombic repulsion energy of each pair of electrons. Since ${}^2\hat{K}$ depends on the coordinates of only two electrons, it may be moved outside the integration over particles 3 to N in Eq. (1), leaving

$$E = \int {}^2\hat{K}\left[\int \Psi(\mathbf{1},\mathbf{2},\ldots,\mathbf{N})\Psi^*(\mathbf{1}',\mathbf{2}',\ldots,\mathbf{N})d3\cdots d\mathbf{N}\right] \times \delta_{\mathbf{1},\mathbf{1}'}\delta_{\mathbf{2},\mathbf{2}'}d\mathbf{1}\,d\mathbf{2}. \qquad (3)$$

The bracketed integration defines the 2RDM. Therefore, we may write the ground-state energy as a linear functional of the 2RDM:

$$E = \int {}^2\hat{K}\,{}^2D(\mathbf{1},\mathbf{2};\mathbf{1}',\mathbf{2}')\delta_{\mathbf{1},\mathbf{1}'}\delta_{\mathbf{2},\mathbf{2}'}d\mathbf{1}\,d\mathbf{2} = \mathrm{Tr}({}^2\hat{K}\,{}^2D). \qquad (4)$$

Importantly, since Eq. (2) contains no approximation, Eq. (4) is exact, and the 2RDM contains all information necessary to compute atomic and molecular energies. Expression of the energy as a linear functional of the 2RDM suggested that straightforward variational minimization over all 2RDMs should yield the correct ground-state energy. However, early optimizations produced energies significantly below the correct values because not every 2RDM corresponds to a real, N-electron wave function. Thus, the minimization must be constrained to ensure that the laws of quantum mechanics are not violated. In 1963, Coleman [19] coined the characterization of these constraints the *N-representability problem.*

In order to avoid constrained minimization, Bopp diagonalized the reduced Hamiltonian. The resulting eigenfunctions are fundamental two-body functions of the Hamiltonian, called eigengeminals in this paper for convenience.

When we need to discuss other sets of two-electron functions, we will use the less restrictive term geminal [20]. In the diagonal representation, Eq. (4) is rewritten as

$$E=\sum_{n} p_n \epsilon_n, \tag{5}$$

where p_n are the diagonal elements of ${}^2D$ in the representation that diagonalizes ${}^2\hat{K}$, and the sum runs over all eigengeminals in the system. Off-diagonal elements of ${}^2D$ in this representation vanish in Eq. (5) because they do not contribute to the energy. Physically, we may interpret the p_n as occupation numbers for the eigengeminals, where the quasiparticles that occupy these functions are often called pairons [21,22]. Then, imposing N-representability on ${}^2D$ is replaced by selecting an appropriate, normalized distribution for the eigengeminal energy weightings p_n in order to yield an accurate ground-state energy of the system.

Equation (5), which is still exact, is tantalizing because it expresses the ground-state energy in exactly the same way as one might approach a system of independent particles. Of course, exact knowledge of the p_n is tantamount to knowledge of the wave function itself, so use of Eq. (5) for electronic structure calculations requires an approximation for the p_n. To this end, Bopp used Eq. (5) to formulate a lower bound for the ground-state energy by assuming that the lowest-energy eigengeminals are fully occupied ($p_n=1$) and the remaining eigengeminals unoccupied. The bound was later corrected by Coleman [19], but even including this correction, the bound is poor for systems with more than a few electrons. Following Bopp's work, Grimley and Peat formed simple approximations to the p_n: first by considering symmetry interactions of the eigengeminals with 2×2 Slater determinants of the occupied Hartree-Fock orbitals [23], and later by relating the occupation numbers to infinite-order perturbation theory [24]. Their efforts yielded energies with about 2% accuracy, but only for a series of few-electron ions. Coleman also considered forming an approximation to the occupation numbers by minimizing the informational entropy contained in the p_n [22], yielding a formula for the p_n related to the Boltzmann distribution. With this approach, Coleman obtains good accuracy, but only for a harmonic-type Hamiltonian with no external forces (i.e., nuclei) and nonphysical, power-law potentials.

Several authors have subsequently investigated the concepts of many-electron populations [21,25–28]—especially in light of the discovery of Cooper pairing in superconductors [29]. Use of electron-pair states and their energies is also well known in the quantum-chemical literature, perhaps most famously in the antisymmetrized geminal power methods [30–32]. However, for all these electron-pair efforts, few researchers examined Bopp's approximation again. Yet the equation is so simple that an approach based on approximating the occupation numbers would be a welcome addition to the electronic structure literature if it could provide a reasonable degree of accuracy in a computationally efficient way [23,33]. This idea is fundamentally different from previous attempts at using electron-pair states as a basis for quantum-chemical calculations.

The present paper resumes this line of research by introducing an approximation for the eigengeminal occupation numbers based on Fermi-Dirac (FD) statistics of individual electrons. This approach introduces a temperature parameter T, unrelated to any thermodynamic quantity, in order to determine the p_n. As a result, the system energy E_{PDF} becomes a function of T. The temperature parameter may be thought of as a measure of correlation in the system (thus, we will henceforth refer to it as the "correlation temperature"). It will be shown in Sec. II that the zero of correlation temperature implies zero electronic correlation, and increasing the correlation temperature incorporates further electronic correlation in the system. However, in an interesting reversal, because the occupation numbers p_n are paired against the correlated two-electron energies of the system, too little electronic correlation in the occupation numbers will actually lead to an energy *below* the true ground-state energy of the system. Thus, $E_{\mathrm{PDF}}(T=0)$ is a modified Bopp bound on the ground-state energy in the sense that it approximates the energy by simply summing the eigenvalues of ${}^2\hat{K}$, but selects *which states to include in the sum* in accord with our formula for p_n. By itself, $E_{\mathrm{PDF}}(0)$ is a tremendous improvement on Bopp's initial lower bound for the energy. However, the flexibility afforded by the correlation temperature means that at some critical temperature $T^*>0$, $E_{\mathrm{PDF}}(T^*)$ produces the true-ground-state energy. Because the energies ϵ_n (eigenvalues of ${}^2\hat{K}$) incorporate electronic correlation through infinite order, electron correlation is an innate feature of $E_{\mathrm{PDF}}(T)$. Increasing the correlation temperature plays a key role in removing overcorrelation in order to achieve the correct energy.

An ultimate goal of this research is to make *a priori* predictions at T^* in order to approximate the ground-state energies of atoms and molecules via the pairon distribution function method. In this initial paper, however, we will be more modest. The primary goal of this paper is to establish a formula for the p_n based on the FD statistics of individual electrons, and to show that the formula we propose is a reasonable zeroth-order estimate to the true pairon distribution function. Then, by using a simple geometric argument based on the empirical properties of the $E_{\mathrm{PDF}}(T)$ curve as a predictive barometer, we will show that our formula for the p_n can produce reasonable estimates to the ground-state energies of atoms and molecules.

The remainder of this paper is organized in the following way. Section II details the theoretical foundations of this approach, with an emphasis on why the statistics of individual electrons should form a reasonable approximation to the occupation numbers p_n. Section III then lays out the computational details used in this research in modest detail. Characteristic results are displayed in Sec. IV with accompanying discussion. Finally, in Sec. V we comment on useful ways this method may be improved in the future.

II. THEORY

Since Eq. (5) is so simple, an electronic structure calculation based on approximating the occupation numbers p_n would be welcome if it could predict ground-state energies in a reasonably accurate and computationally inexpensive way. At the same time, any attempt at using Eq. (5) for computational purposes must respect the behavior of the eigengeminal occupation numbers in atoms and molecules. It is found that the eigengeminal occupation numbers bear no clear relationship to the two-particle energies. For example, in the limit of zero electronic correlation (Hartree-Fock picture), the filling has some unoccupied eigengeminals mixed into the occupied eigengeminals, even though the orbitals are occupied strictly in order of their energy. We refer to this phenomenon as "swiss-cheese" occupation of the eigengeminals. As more electronic correlation is included in the system, the occupation numbers move away from zero and unity but the overall pattern of marginally occupied eigengeminals interspersed with strongly occupied eigengeminals remains. Any theory attempting to approximate the occupation numbers statistically should include a reasonable, qualitative recreation of the swiss-cheese behavior.

Previous attempts at using Eq. (5) fail to take account of swiss-cheese eigengeminal occupation. In particular, Bopp tried simply summing the $\binom{N}{2}$ lowest eigenvalues of ${}^2\hat{K}$ [14]. The approach essentially treats the two-electron space in the same way one applies the *Aufbau* principle in molecular-orbital theory; as a result, his theory is guaranteed *not* to reproduce the qualitative behavior of the eigengeminal occupation numbers at *any* degree of electronic correlation. In other words, it never reproduces the swiss-cheese occupation, even at the Hartree-Fock limit. Even after correction by Coleman [19], Bopp's approach has two main flaws: (i) in the noninteracting pairon limit, it fails to reproduce the uncorrelated (Hartree-Fock) energy, and (ii) the lower bound is so weak as to render it entirely useless. On the other hand, Coleman's own attempt [22] at employing Eq. (5) uses Boltzmann-type statistics to approximate the p_n. While innovative, this method is limited in the sense that it does not reproduce well the qualitative behavior of the occupation numbers in atomic and molecular systems.

Coleman's introduction of a statistical distribution function into Eq. (5) motivates our own theory. The chief problem with two-particle statistics is that interacting pairons obey no known distribution function [21,22]. In this article, we assume that FD statistics closely model the population of the individual electrons in an interacting system. The key advance we present here is how to combine the one-electron populations appropriately in order to generate our zeroth-order estimation to the eigengeminal occupation numbers.

To make our analysis easier to follow, we proceed by analogy with the familiar one-electron picture of a correlated system of electrons, first suggesting how to apply the idea of electron statistics to a one-electron picture of a system and then moving that idea to a two-electron picture. Consider a typical self-consistent-field Hartree-Fock calculation, where the ground-state energy is obtained by summing the energies of the lowest N Fock spin orbitals, less a correction for double counting of the electron-electron interaction energy [34]. We incorporate the statistical-mechanical concept of a distribution function into the one-electron picture by assigning electrons to the Fock orbitals in accordance with the FD distribution. In *one-electron* FD statistics, the population n_k of the kth energy level is determined by its energy ϵ_k, the chemical potential μ, and the temperature T as

$$n_k(T,\mu) = \frac{1}{e^{(\epsilon_k-\mu)/T}+1}, \tag{6}$$

where Boltzmann's constant k_B has been subsumed into T to tidy up the notation [35]. At the $T=0$ limit, FD statistics regenerate Hartree-Fock filling of the spin orbitals because all orbitals will have occupations of either 1 or 0, depending on where ϵ_k lies relative to μ. Thus the N lowest-energy orbitals will be occupied, with the rest empty.

In the two-electron picture, it remains to devise an appropriate pairon distribution function for the geminal energy states. Bopp's theory is a clear two-electron analog of Hartree-Fock-style filling of the Fock spin orbitals. To move away from this limit, consider again the Fock spin orbitals, ordered from lowest energy to highest energy and occupied by N electrons according to the FD distribution. Forming geminals from pairwise, antisymmetric combinations of these orbitals (an orbital-product basis) leads to an unusual arrangement of geminal energies and occupations. For example, a geminal formed from a very low-energy, occupied orbital and a low-lying, unoccupied (virtual) orbital might actually have a composite energy *lower* than a geminal formed from two high-energy occupied orbitals. Yet the higher-energy geminal, derived from two occupied orbitals, should have greater occupation than the lower-energy geminal because the latter state is partially formed from an unoccupied (or only slightly occupied, in the $T>0$ case) orbital. This physical arrangement of geminal energies and occupations suggests that there exists no definite Fermi level (chemical potential) in the two-particle space. Instead, there should be a gray area where geminal population does not monotonically decrease with increasing geminal energy. In this region, the energy of the geminal states and their occupation numbers are not closely correlated. Precisely this behavior is observed in the occupation numbers of true N-representable 2RDMs.

Based on this qualitative description of the occupation numbers, we propose constructing the pairon distribution function as a tensor product of two one-electron distributions, each determined by the Fock energies of the component orbitals and in accordance with FD statistics for each individual electron. Therefore, we construct a diagonal pairon population matrix ${}^2P$ with potentially nonzero matrix elements

$${}^2P^{i,j}_{i,j}(T) = \sigma_{i,j} n_i(T,\mu) n_j(T,\mu), \tag{7}$$

where n_i and n_j are defined by Eq. (6). The occupation numbers p_n are defined by the diagonal elements of ${}^2P$, where the compound indexing on the matrix in Eq. (7) reflects that each geminal is formed from the antisymmetric combination of two orbitals. The factor $\sigma_{i,j}$ is a symmetry coefficient. In simple molecular systems with high degrees of symmetry, the occupations of certain eigengeminal states are rigorously zero due to orthogonality against the ground state. This feature of the two-electron occupation numbers cannot be accounted for by the FD distribution alone, and so $\sigma_{i,j}=0$ if the

i,j-th eigengeminal is forbidden, and unity otherwise. The chemical potential disappears from the left-hand side of Eq. (7) because, as a one-electron property, it has no direct meaning in the two-particle space; instead, we use it as a parameter to normalize the ${}^2P$ matrix. In addition, it is important to point out that ${}^2P$ is not an N-representable 2RDM. Off-diagonal elements of ${}^2P$, omitted in Eq. (7) because they do not contribute to the energy, affect the N-representability of the matrix. Since the pairon distribution function method is not variational, N-representability is not examined here in the same fashion as in other work [10,13]. Instead, the issue is addressed by using T to tune the eigengeminal occupation numbers.

Explicitly substituting Eq. (7) into Eq. (5) yields

$$E_{\mathrm{PDF}}(T) = \sum_n {}^2P_n^n(T)\epsilon_n, \tag{8}$$

which parametrizes the energy generated through the pairon distribution function approach by the correlation temperature T. Our expression for ${}^2P$ marks the first approximation in an analysis that has heretofore been exact. Therefore, the validity of Eq. (7) alone will impact the accuracy obtained via Eq. (8).

Within the approximation, consider the expected behavior of Eq. (8). In the $T=0$ limit, the orbital populations n_k reduce to either 0 or 1; therefore, each p_n will be unity if and only if it corresponds to two occupied orbitals. This is the zero-correlation limit for the occupation numbers in the two-electron space. A comforting feature of our model pairon distribution function is that taking the $T=0$ p_n as weights against the diagonal elements of ${}^2\hat{K}$ renders the Hartree-Fock energy, confirming that our ansatz for the pairon distribution function assigns geminal population appropriately. If we diagonalize ${}^2\hat{K}$ and take the same $T=0$ p_n as weights against the resulting eigenvalues, the resulting energy is below the Hartree-Fock energy because the eigengeminal energies are generally lower than the diagonal elements of ${}^2\hat{K}$. Therefore, the $T=0$ behavior is akin to Bopp's approximation in the sense that the eigengeminals will be either fully occupied or unoccupied, but with the essential modification that the contributing states correspond to two occupied orbitals rather than the eigengeminal states lowest in energy. By controlling which eigengeminals are populated in the zero-correlation limit, $E_{\mathrm{PDF}}(0)$ is a tremendous improvement on the Bopp lower bound for the ground-state energy. As T increases, $E_{\mathrm{PDF}}(T)$ should also generally increase because population is being transferred mainly from low-energy states to higher-energy states. In practice, this increase is typically monotonic for systems of moderate size ($N\sim 10$).

III. COMPUTATIONAL DETAILS

A. Basis sets and spin adaptation

In the following calculations, ${}^2\hat{K}$ is built using the one- and two-electron integrals output by the GAMESS software package [36]. Reference energies are also obtained via GAMESS; where full configuration interaction (FCI) is computationally infeasible, coupled-cluster singles-doubles with perturbative triples [CCSD(T)] energies are used as a substitute. All geometries are obtained via Ref. [37]. The basis sets used are either native to GAMESS or imported through the Extensible Computational Chemistry Environment Basis Set Database [38]. These basis functions are then spin adapted (i.e., taken in linear combination in order to become eigenfunctions of both $\hat{S}^2$ and $\hat{S}_z$), which leads to two distinct 2RDM spin blocks: a singlet block ($S=0$) and a triplet block ($S=1$) [39]. The spin-adaptation procedure transforms Eq. (8) into

$$E_{\mathrm{PDF}}(T) = \sum_n {}^{2(s)}\hat{P}_n^n(T)\ {}^{(s)}\epsilon_n + 3\sum_n {}^{2(a)}\hat{P}_n^n(T)\ {}^{(a)}\epsilon_n, \tag{9}$$

where the left superscript (s) denotes the symmetric, singlet block and the left superscript (a) indicates the antisymmetric, triplet block. These blocks are of dimension $r(r+1)/2$ and $r(r-1)/2$, respectively, where r is the number of spatial orbitals in the system. The eigengeminals ${}^{(s)}\epsilon_n$ and ${}^{(a)}\epsilon_n$ are obtained by spin-adapting ${}^2\hat{K}$ and diagonalizing the individual blocks separately. The spin-adaptation procedure causes the two blocks of the 2RDM to have different traces [39]; therefore, the blocks of ${}^2P$ in Eq. (9) must also have different traces. To accomplish this requirement in the context of Eq. (7), at a given temperature ${}^{2(s)}\hat{P}$ and ${}^{2(a)}\hat{P}$ are constructed from the same Fock orbital energies but with different chemical potentials.

B. Orbital-geminal mapping

Central to the pairon distribution function approximation is the ability to define a one-to-one mapping between the each eigenfunction of ${}^2\hat{K}$ and the two Fock orbitals that form it. Equations (8) and (9) are not helpful without such a mapping because Eq. (7) uses one-electron energies to produce two-electron populations. Thus, we must identify a way to pair each eigenvalue of ${}^2\hat{K}$ uniquely with an antisymmetric combination of the Fock orbitals. Ambiguity in this mapping violates the fundamental premise behind our pairon distribution function.

Consider a correlation parameter χ that smoothly morphs the reduced Hamiltonian from the Fock limit to fully correlated limit. The effective reduced Hamiltonian ${}^2\tilde{K}$, parametrized as a function of χ, looks like

$${}^2\tilde{K}(\chi) = (1-\chi)\,{}^2\hat{F} + \chi\,{}^2\hat{K}, \quad \chi \in [0,1], \tag{10}$$

where ${}^2\hat{F} = {}^1\hat{F} \wedge {}^1I$ is the two-particle Fock energy matrix and ${}^2\hat{K}$ is, as before, the reduced Hamiltonian generated from the one- and two-electron integrals of the Fock spin orbitals. Diagonalization of ${}^2\tilde{K}$ at any χ will yield the eigengeminals for a particular degree of correlation, with the eigengeminals at $\chi=0$ corresponding to the Fock geminals (antisymmetrized products of the Fock orbitals) and the eigengeminals at $\chi=1$ corresponding to the fully correlated eigengeminals of the system.

In order to create an accurate mapping between the eigenvalues of ${}^2\hat{K}$ and the component Fock orbitals, we discretize

TABLE I. Bopp's lower bound and the $T=0$ pairon distribution function energy for a series of simple molecules, compared to the full configuration-interaction energy. Results are tabulated for a Dunning-Hay basis (DH) and a correlation-consistent polarized double-ζ basis (cc-pVDZ); all energies are in hartrees. The pairon distribution function approximation is a substantial improvement on Bopp's crude lower bound, suggesting that geminal population is assigned correctly in the $T=0$ limit.

	D-H			cc-pVDZ		
Molecule	E_{Bopp}	$E_{\text{PDF}}(0)$	E_{FCI}	E_{Bopp}	$E_{\text{PDF}}(0)$	E_{FCI}
Be	−16.697	−14.860	−14.616	−16.766	−14.945	−14.619
Be_2	−39.629	−34.095	−29.222	−39.950	−34.580	−29.234
H_2O	−143.637	−82.678	−76.140	−153.316	−83.728	−76.244
CH_4	−83.616	−45.210	−40.299	−84.757	−46.196	−40.389
N_2	−182.937	−130.394	−109.097	−186.280	−132.046	−109.274

χ in n intervals ($\chi_0=0$ and $\chi_{n-1}=1$) and consider the series of products $V_{j-1}^{\mathrm{T}}V_j$, where V_j is the similarity transform that diagonalizes ${}^2\widetilde{K}(\chi_j)$. Clearly, as $n\rightarrow\infty$, $V_{j-1}^{\mathrm{T}}V_j=I$. However, for finite n, the matrix $V_{j-1}^{\mathrm{T}}V_j$ consists of one dominant entry in each row and column, with the remaining elements small. Dominant off-diagonal elements in this matrix product indicate where the eigenvalues of ${}^2\widetilde{K}(\chi_j)$ have changed ordering relative to those of ${}^2\widetilde{K}(\chi_{j-1})$. If we define a matrix rounding function $\lfloor\cdot\rceil$ that rounds the dominant terms in a row and column of a matrix to unity and all other elements to zero, the matrix product $\lfloor V_{j-1}^{\mathrm{T}}V_j\rceil$ becomes a permutation matrix labeling the changes in the ordering of the eigenvalues from one point in χ to the next. Then, by accumulating these permutation matrices via the recurrence relation

$$\Phi_j=\Phi_{j-1}\lfloor V_{j-1}^{\mathrm{T}}V_j\rceil, \quad \Phi_0=V_0, \tag{11}$$

where Φ_j is a permutation matrix, we ensure that the eigenvalues of $\Phi_j\,{}^2\widetilde{K}(\chi_j)\Phi_j^{\mathrm{T}}$ are ordered consistently with the Fock geminal matrix ${}^2\hat{F}$. Note that Φ_0 is itself a permutation matrix because ${}^2\widetilde{K}(\chi_0)$ is a diagonal matrix.

In the following calculations, the mappings between the eigengeminals of ${}^2\hat{K}$ and the Fock orbitals are obtained by diagonalizing ${}^2\widetilde{K}$ at every discretized value of χ and accumulating Φ_n. In general, n ought to increase with the size of the system because bigger matrices contain the possibility of more ordering changes, requiring a finer mesh to capture the proper ordering. At the same time, the energies (both one- and two-particle) tend to grow closer together in large systems, so capturing each individual ordering change becomes less important to the overall energy. In practice, we found $n\approx10^2$ is a good compromise.

IV. CHARACTERISTIC DATA, RESULTS, AND DISCUSSION

In this section, we detail some immediate results obtained from our pairon distribution function when inserted in Eq. (5) and display results typical of small molecules. All results are calculated at $\chi=1.0$, where all electronic correlation is included.

A. Bopp approximation vs pairon distribution approximation

The key distinction of the pairon distribution function approach from Bopp's approximation is that the eigengeminals of ${}^2\hat{K}$ are occupied in accord with a tensor product of the one-electron populations of the component Fock orbitals. The resulting p_n form a nontrivial pattern for the eigengeminal occupation numbers that blurs the concept of a Fermi level in the two-electron space. The difference is clearly illustrated by comparing the Bopp approximation energy to $E_{\text{PDF}}(0)$ energy; although both approximations use only completely occupied and completely unoccupied eigengeminals, the choice of *which* states get population has a dramatic effect on the energy.

These energies are displayed for several simple molecules in Table I. As the number of electrons grows beyond four, Bopp's approximation deteriorates rapidly, in some cases leading to a lower bound more than twice as low as the true ground-state energy. Researchers abandoned work along the lines of this approximation in the 1960s because it was thought that Bopp's bound was simply too low to be useful. Conversely, the $T=0$ pairon distribution function approximation is closer to the true energy, consistently about 10% below the ground-state energy—which is remarkable considering the simplicity of the methodology. Selectively choosing which eigengeminals receive pairon population dramatically improves estimation of the ground-state energy, and suggests that the tensor product concept has merit as a means to distribute pairon population in the system.

B. Characteristic behavior of $E_{\text{PDF}}(T)$

Although $E_{\text{PDF}}(0)$ represents a huge improvement over the Bopp approximation, the temperature parameter introduces tremendous flexibility into the pairon distribution function method. Figure 1 displays one $E_{\text{PDF}}(T)$ curve against both the Hartree-Fock and FCI energies. The behavior is characteristic of most small molecules with about ten electrons.

Some immediate features emerge from Fig. 1. First, the Hartree-Fock energy corresponds to the highest temperature, with successive (more correlated) energies intersecting $E_{\text{PDF}}(T)$ at lower temperatures. This is somewhat opposite a

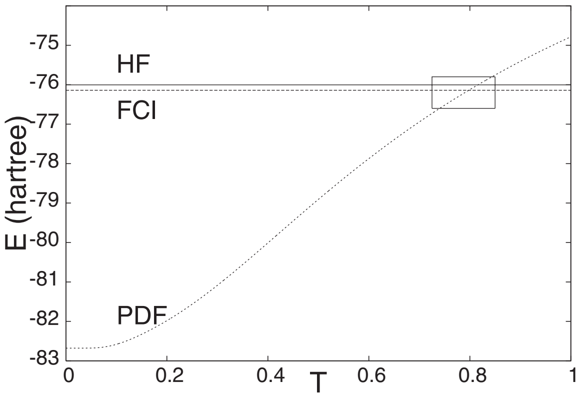

FIG. 1. $E_{\mathrm{PDF}}(T)$ (dotted curve) plotted for H_2O in a Dunning-Hay basis along with the Hartee-Fock and FCI energies (solid and dashed lines, respectively). The curve is typical for small molecules with ~10 electrons. Note that $E_{\mathrm{PDF}}(0)$ is a much improved lower bound on the true energy over the Bopp bound, which is too low to be shown. Importantly, in the region of energetic interest (boxed), $E_{\mathrm{PDF}}(T)$ has a positive first derivative and negative second derivative, with higher derivatives continuing to alternate in sign.

typical quantum chemist's view of the Hartree-Fock (HF) picture; in a configuration-interaction understanding of quantum chemistry, inclusion of excitations from the HF determinant leads to lowering of the overall energy. However, in terms of electron statistics, excitations from the HF wave function are associated with an increase in temperature. Thus one might reasonably connect increasing temperature with lowering of the overall energy, but Fig. 1 displays precisely the opposite. How can we remedy the apparent paradox? The key to understanding Fig. 1 lies in how electron correlation enters into $E_{\mathrm{PDF}}(T)$. Recall that the factors influencing each p_n are the Fock spin orbital energies of each component orbital, as well as the temperature. Since the Fock orbital energies essentially define the uncorrelated system energy, the occupation numbers do not contain any information regarding correlation in the system. This is one reason why they may be used in the $T=0$ limit to obtain the Hartree-Fock energy. Instead, E_{PDF} captures electronic correlation because it performs a weighted sum of the eigenvalues of $^2\hat{K}$, which are the fully correlated, two-electron energies of the system.

Second, in the region of energetic interest (i.e., in the neighborhood of the true ground-state energy and the Hartree-Fock energy; in Fig. 1, this region is boxed), $E_{\mathrm{PDF}}(T)$ is observed to have a positive first derivative and negative second derivative, with higher derivatives continuing to alternate in sign. This is an important property of the curve that is potentially useful if the pairon distribution function method is to be used in a predictive way.

For example, consider expanding $E_{\mathrm{PDF}}(T)$ in a first-order Taylor series $\bar{E}(T)$ about the temperature that yields the Hartree-Fock energy, T_{HF}. Determination of this temperature may be accomplished numerically without any knowledge of the true energy of the system. Due to the curvature of $E_{\mathrm{PDF}}(T)$, the first-order Taylor expansion at this point will always lie above the true curve in this region. In other words, at any temperature $T<T_{\mathrm{HF}}$ in this region, $\bar{E}(T)>E_{\mathrm{PDF}}(T)$.

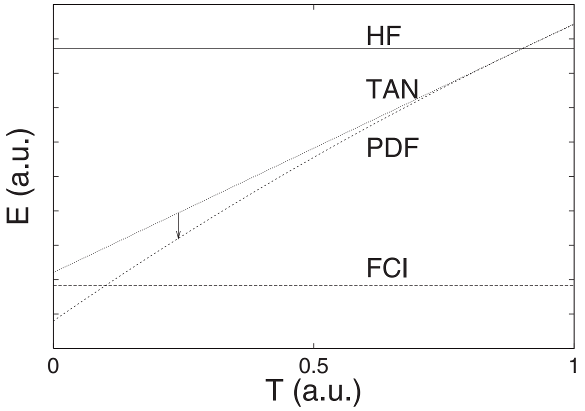

FIG. 2. Schematic representation of $E_{\mathrm{PDF}}(T)$ in the region of the Hartree-Fock and FCI energies, as boxed in Fig. 1. In real molecules, the Taylor expansion of the curve, denoted TAN, is far closer to the true curve than shown here. Blowing up the region displays the effect of using the Taylor expansion to predict the critical temperature. By finding the intersection of the tangent line with a characteristic energy (in this paper, this CISD energy), following the arrow to the true curve results in a lowering of the overall energy.

Figure 2 schematically depicts this geometric relationship for a fictional molecule.

The remaining issue is how to arrive at a suitable T such that $E_{\mathrm{PDF}}(T)$ is a good approximation to the true ground-state energy. Our initial—but by no means definitive—suggestion is to use characteristic energies of the system that fall between the Hartree-Fock and FCI energies as references in order to calibrate a Taylor-like expansion of the energy. Any variational electronic structure method will serve this purpose because it is guaranteed to be an upper bound to the true energy; for simplicity, we elect to use truncated configuration interaction methods, particularly with single and double excitations (CISD), as our reference. By finding the temperature at which the CISD energy intersects $\bar{E}(T)$ and then plugging that temperature into $E_{\mathrm{PDF}}(T)$, the curvature of $E_{\mathrm{PDF}}(T)$ guarantees we obtain a new, lower energy. In Fig. 2, this procedure corresponds to dropping a vertical line between the Taylor expansion and the true energy curve at the temperature where $\bar{E}(T)$ meets the CISD energy, and reading off the new estimate from $E_{\mathrm{PDF}}(T)$.

The amount of improvement in the energy estimate depends on both the curvature of $E_{\mathrm{PDF}}(T)$ relative to its first-order Taylor expansion as well as the accuracy of the input (reference) energy. Greater curvature in $E_{\mathrm{PDF}}(T)$ (i.e., away from the first-order Taylor expansion) will lead to a more dramatic energy-lowering effect when going from the Taylor expansion to the real curve. At the same time, if the reference energy is *too* close to the true energy, it is possible to overshoot the true energy and predict a value that is too low—regardless of the curvature of $E_{\mathrm{PDF}}(T)$. For this reason, we submit that the CISD energy is a good reference energy to use because for nonminimal basis sets the CISD value is always far enough from the true energy that estimating the ground-state energy with this method should rarely produce an energy too low. A slight modification of this procedure is

TABLE II. The pairon distribution function energies (as percentages of the correlation energy) and temperatures are tabulated for a few small molecules with prediction factor $f=0.999$. The reference CISD energy is also shown. The predicted energy improves as the basis size increases, predominantly because the reference energy is further from the true energy.

	D-H			cc-pVDZ		
Molecule	E_{CISD}	T	$E_{\mathrm{PDF}}(T)$	E_{CISD}	T	$E_{\mathrm{PDF}}(T)$
H_2O	96.15	0.7978	101.78	96.20	0.8405	100.88
CH_4	96.04	0.6164	101.20	95.58	0.6253	99.76
NH_3	94.46	0.7303	99.93	95.79	0.7355	100.27
HF	95.48	0.8649	101.71	97.36	0.9629	102.36
N_2	93.02	1.8320	98.26	93.22	1.6823	98.66

to multiply the temperature at which $\bar{E}(T)$ meets the reference energy by a prediction factor $f \lesssim 1$, and then approximate the ground-state energy with $E_{\mathrm{PDF}}(fT)$. While this approach requires an empirical determination of f, it can produce a bigger difference in energy between $\bar{E}(T)$ and $E_{\mathrm{PDF}}(T)$. Use of a prediction factor is particularly useful if the curvature of the pairon distribution function curve is slight compared to its Taylor expansion.

Table II shows the CISD reference energy and the pairon distribution function predicted energy (as percentages of the correlation energy) for a series of simple molecules in two basis sets. A prediction factor of $f=0.999$ is used because empirically it has been determined to yield favorable results. Table II shows that the predictive algorithm outlined above does improve on the CISD energy by a few percent of the correlation energy. The prediction is generally better as the size of the basis increases because in these cases the CISD energy is further away from the true energy, and thus there is less chance of the predicted energy falling below the true energy. The factor f plays a critical role in the accuracy of the predicted energy. In medium-size bases (Dunning-Hay, correlation-consistent polarized double ζ), the CISD energy is far enough from the true energy that when f is unity, the resultant energy (not shown) still needs accuracy improvement. The same situation arises when the curvature of $E_{\mathrm{PDF}}(T)$ is slight, and the Taylor expansion $\bar{E}(T)$ follows the curve closely. In these cases, $f<1$ acts to lower the energy just enough to bring it a few percent of the correlation energy closer to the true energy.

The authors make no claim that the predictive method described above is optimal; in fact, it is likely that with further investigation, additional properties of $E_{\mathrm{PDF}}(T)$ will emerge that should make predicting the true ground-state energy a more exact procedure. Even without additional information, clever algorithms may be able to determine the temperature where $E_{\mathrm{PDF}}(T)$ meets the FCI energy without need for an empirical parameter f.

V. CONCLUSIONS AND FUTURE WORK

In this paper, we propose approximating the ground-state energy of atoms and molecules as a weighted sum of the eigenvalues of its two-particle reduced Hamiltonian ${}^2\hat{K}$. The weights for each eigengeminal may be interpreted as occupation numbers for each two-particle energy level. While researchers have considered using this approach previously—most famously by Bopp—the present article introduces the key development of modeling the geminal occupation numbers p_n with a tensor product of two one-electron FD distributions. This functional form of the eigengeminal occupation numbers is attractive for several reasons. First, at energies of chemical interest, the p_n qualitatively resemble the true diagonal elements of 2RDMs. Instead of exhibiting a clear Fermi level, the p_n display the swiss-cheese filling pattern we know is present in true 2RDMs. Second, the p_n as constructed in this paper have useful limiting behavior in the $T=0$ limit because they all reduce to 0 or 1. When taken as weights against the diagonal elements of ${}^2\hat{K}$, they render the Hartree-Fock energy; when taken as weights against the *eigenvalues* of ${}^2\hat{K}$, they produce a much-improved Bopp bound on the energy.

The pairon distribution function introduces a correlation temperature T, unrelated to any thermodynamic quantity, that parametrizes the occupation numbers and consequently the overall energy of the system. The parametrization creates a function $E_{\mathrm{PDF}}(T)$ that, at some critical temperature T^*, matches the true ground-state energy. The properties of the pairon distribution function energy curve suggest a simple geometric construction, based on a Taylor series about the Hartree-Fock temperature, as a basis for predicting T^* and consequently the true ground-state energy. This procedure requires a reference energy in order to focus on the region of $E_{\mathrm{PDF}}(T)$ near the critical temperature. Variational upper bounds to the true energy work best for this purpose because the predictive procedure implemented in this paper relies on lowering the energy from the Taylor series to the real curve. Other predictive algorithms are possible, and a likely future direction of this research is the development of more accurate and reliable means of using $E_{\mathrm{PDF}}(T)$ predictively. One option may be constructing several Taylor series at different points along $E_{\mathrm{PDF}}(T)$, and using these approximations to bracket the true energy within some window. These series could be centered either at other characteristic energies of the system (e.g., Møller-Plesset energies or other truncated CI methods) or at nonphysical points on the curve, like its inflection point.

Another future direction of the present research is generalizing Eq. (7) to be able to account for highly correlated systems that exhibit fermionic pair condensation ($p_n > 1$), like superconductors. While most standard electronic structure methods cannot treat such exotic electronic systems, the flexibility of Eq. (5) makes such calculations tractable. It remains to develop an appropriate formula for the p_n that captures pair condensation phenomena but still reduces to the desired swiss-cheese filling for more standard electronic structure problems.

The pairon distribution function method is appealing because it introduces a new way of thinking of electron correlation in atomic and molecular systems. In the two-electron space, all correlation is taken into account, without approximation, by diagonalization of ${}^2\hat{K}$. The ground-state energy is produced by adding together the eigengeminals of the reduced Hamiltonian according to their population. Thus the electronic structure problem reduces to assigning pairon population appropriately, which we do in this paper by a tensor product of two one-electron distributions. In this sense, we feel the pairon distribution function method complements DFT, natural-orbital functional theory, and other pair functional theories. Approximating the geminal occupation numbers is clearly a physical process for which quantum chemists' intuition will be a great asset in further research. With additional work, we believe that the pairon distribution function method should be able to yield reasonably accurate ground-state energies at minimal computational cost.

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[1] D. ter Haar, Rep. Prog. Phys. **24**, 304 (1961).
[2] C. A. Coulson, Rev. Mod. Phys. **32**, 170 (1960).
[3] P. O. Löwdin, Phys. Rev. **97**, 1474 (1955).
[4] D. A. Mazziotti, Phys. Rev. Lett. **97**, 143002 (2006).
[5] D. A. Mazziotti, Phys. Rev. A **75**, 022505 (2007).
[6] D. A. Mazziotti, in *Reduced-Density-Matrix Mechanics: With Application to Many-Electron Atoms and Molecules*, edited by D. A. Mazziotti, Advances in Chemical Physics Vol. 134 (John Wiley and Sons, New York, 2007), pp. 332–342.
[7] D. A. Mazziotti, J. Chem. Phys. **126**, 184101 (2007).
[8] R. Erdahl, Rep. Math. Phys. **15**, 147 (1979).
[9] D. A. Mazziotti, Phys. Rev. Lett. **93**, 213001 (2004).
[10] D. A. Mazziotti, Phys. Rev. A **65**, 062511 (2002).
[11] G. Gidofalvi and D. A. Mazziotti, J. Chem. Phys. **122**, 094107 (2005).
[12] Z. Zhao, B. J. Braams, M. Fukuda, and M. L. Overton, J. Chem. Phys. **120**, 2095 (2004).
[13] D. A. Mazziotti, Phys. Rev. A **74**, 032501 (2006).
[14] F. Bopp, Z. Phys. **156**, 348 (1959).
[15] *Reduced-Density-Matrix Mechanics: With Application to Many-Electron Atoms and Molecules*, edited by D. A. Mazziotti (Ref. [6]).
[16] S. Goedecker and C. J. Umrigar, in *Many-Electron Densities and Reduced Density Matrices*, edited by J. Cioslowski (Kluwer Academic/Plenum Publishers, New York, 2000), pp. 165–181.
[17] D. A. Mazziotti, J. Chem. Phys. **112**, 10125 (2000).
[18] M. Piris, Int. J. Quantum Chem. **106**, 1093 (2006).
[19] A. J. Coleman, Rev. Mod. Phys. **35**, 668 (1963).
[20] H. Shull, J. Chem. Phys. **30**, 1405 (1959).
[21] A. J. Coleman, Int. J. Quantum Chem. **13**, 67 (1978).
[22] A. J. Coleman, E. P. Yukalova, and V. I. Yukalov, Int. J. Quantum Chem. **54**, 211 (1995).
[23] T. B. Grimley, Proc. Phys. Soc. London **84**, 178 (1964).
[24] T. B. Grimley and F. D. Peat, Proc. Phys. Soc. London **86**, 249 (1965).
[25] R. Ponec and M. Strnad, Int. J. Quantum Chem. **50**, 43 (1994).
[26] P. Karafiloglou, Chem. Phys. **140**, 373 (1990).
[27] R. C. Bochicchio, J. Mol. Struct.: THEOCHEM **228**, 209 (1991).
[28] P. Karafiloglou, Chem. Phys. **128**, 373 (1988).
[29] I. G. Kaplan, O. Navarro, and J. A. Sánchez, Phys. Status Solidi B **242**, 1793 (2005).
[30] A. J. Coleman, J. Math. Phys. **6**, 1425 (1965).
[31] A. J. Coleman, Int. J. Quantum Chem. **63**, 23 (1997).
[32] D. A. Mazziotti, Chem. Phys. Lett. **338**, 323 (2001).
[33] A. J. Coleman, J. Low Temp. Phys. **74**, 1 (1989).
[34] A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory* (Dover Publications, New York, 1982).
[35] D. A. McQuarrie, *Statistical Mechanics* (University Science Books, Sausalito, California, 2000).
[36] M. W. Schmidt *et al.*, J. Comput. Chem. **14**, 1347 (1993).
[37] *Handbook of Chemistry and Physics*, 79th ed., edited by David R. Lide (CRC, Boca Raton, FL, 1998).
[38] Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 02/02/06, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory. Contact Karen Schuchardt for further information.
[39] G. Gidofalvi and D. A. Mazziotti, Phys. Rev. A **72**, 052505 (2005).