Editors' Suggestion

Excitations of Quantum Many-Body Systems via Purified Ensembles: A Unitary-Coupled-Cluster-Based Approach

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State-average calculations based on a mixture of states are increasingly being exploited across chemistry and physics as versatile procedures for addressing excitations of quantum many-body systems. If not too many states should need to be addressed, calculations performed on individual states are also a common option. Here we show how the two approaches can be merged into one method, dealing with a generalized yet *single* pure state. Implications in electronic structure calculations are discussed and for quantum computations are pointed out.

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Determining properties of the excitations in quantum many-body systems is a fundamental problem across almost all sciences. For instance, to explain the mechanism of photosynthesis [1,2], human vision [3], or photovoltaics [4], one should take into account that they are mainly light-induced excited-state processes. The fluctuation properties of quantum spectra play also a crucial role in the characterization of quantum chaos [5,6], new states of matter [7], and more generally in the understanding of the temporal evolution of isolated many-body quantum systems [8]. Yet, while ground-state properties of a wide range of systems can nowadays be determined by rather accurate and computationally manageable methodologies [9,10], methodological developments to efficiently target excited states are highly in demand [11–17].

When interested in studying the energy gaps between the ground and low-lying excited states (the optical gap and multiple neutral excitations being prominent examples thereof) we may focus on the first M eigenstates $\{|\psi_0\rangle, \ldots, |\psi_{M-1}\rangle\}$ of a Hamiltonian H and work with

$$\rho(\boldsymbol{w}) = \sum_{j=0}^{M-1} w_j |\psi_j\rangle\langle\psi_j|. \qquad (1)$$

The real positive weights w_j are nothing else but convenient auxiliary quantities. By minimizing the average energy $\mathcal{E}(\boldsymbol{w}) = \mathrm{Tr}[H\rho(\boldsymbol{w})]$ we can determine the individual states and compute all the relevant properties. The advantage of such a *state-average* calculation lies in the fact that the orthogonality of the individual states can be fulfilled automatically, but the individual states are optimal only on the average. Similarly, by mixing states with different particle numbers, calculation of electron affinities, ionization potentials, and fundamental gaps can be performed. Such ensemble calculations are increasingly being used in traditional and emerging electronic structure methods [18–23]. They are also at the center of (time-independent) density functional [24–32] and density matrix functional [33–37] approaches to excited states.

Alternatively, *state-specific* calculations are also a valid option [38–41]. But addressing states one by one, requires us to satisfy extra orthogonality conditions against previously determined states. If not particularly computationally demanding, these extra conditions can imply a *nonhomogeneous* degradation of accuracy. When this happens, comparisons between *different* states get unbalanced.

Aiming at merging the advantages of state-average and state-specific calculations in one approach, here we show how a state-average calculation can be transmuted into a generalized yet *single* state-specific calculation. The enabling idea is to map the targeted mixed state, $\rho(\boldsymbol{w})$, into a pure state

$$\rho(\boldsymbol{w}) \to |\boldsymbol{0}(\boldsymbol{w})\rangle = \sum_j \sqrt{w_j}\,|\psi_j\rangle \otimes |\tilde{\psi}_j\rangle \qquad (2)$$

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belonging to a "double" Hilbert space $\mathcal{H}\otimes\tilde{\mathcal{H}}$ such that $\mathcal{E}(\boldsymbol{w})=\langle\mathbf{0}(\boldsymbol{w})|H|\mathbf{0}(\boldsymbol{w})\rangle$. When the statistical weights are chosen as $w_j=e^{-\beta E_j}/\sum_j e^{-\beta E_j}$, the state in Eq. (2) is the well-known *thermofield*, introduced by Matsumoto and Umezawa [42,43]. Central to many modern developments in quantum sciences, this purification of the thermal state plays an important role in quantum gravity [44–47], nonequilibrium phenomena [48–53], quantum information [54–56], and quantum chemistry [57,58].

As the key result presented in this Letter, we construct a ***w**-field* such that

$$\mathcal{E}(\boldsymbol{w})=\min_S\langle\mathbf{0}|e^{-S(\boldsymbol{w})}H(\boldsymbol{w})e^{S(\boldsymbol{w})}|\mathbf{0}\rangle, \tag{3}$$

where $|\mathbf{0}\rangle$ stands for the *vacuum* (in the double Hilbert space), $S(\boldsymbol{w})$ is an anti-Hermitian "matrix," and $H(\boldsymbol{w})$ is a unitary transformation of the Hamiltonian H.

Crucially, we show that $S(\boldsymbol{w})$ can be fully specified via the unitary (U) coupled-cluster (CC) ansatz [59]. This CC approach is particularly appealing because it handles the treatment of both finite (like molecules) and extended (like solids) systems [60–63]. Its unitary flavor can also help to solve the challenge of treating equally well dynamical and static correlations within a single approach [64]. Yet the corresponding canonical transformation of the Hamiltonian does not truncate which makes its variational implementation not efficient on conventional classical computers. Remarkably, it was recently shown that the (Trotterized) UCC operator can be prepared at a polynomial cost on a quantum computer [65–68].

Once the minimization in Eq. (3) is performed, the respective eigenstates $|\psi_n\rangle$ can be retrieved by projecting $|\mathbf{0}(\boldsymbol{w})\rangle$ on the noninteracting states to which $|\psi_n\rangle$ can be connected and paired to, say, $|\tilde{\psi}_n^0\rangle$. Thereafter, taking the expectation values of the appropriate physical operators on the retrieved states, any property of individual eigenstates can be accessed. When the focus is just on energies, furthermore, we show below that extraction of the eigenstates can be avoided altogether.

In this Letter, after deriving the outlined key results, we validate the resulting approach on a model system, and conclude touching on main perspectives.

Setting up the framework.—Let us restrict ourselves to spinless fermions with nondegenerate spectrum, for simplicity. Bosonic systems may be dealt with analogously. We also assume that noninteracting states can be connected to interacting states [69]. Inspired by the seminal idea of thermofields [43], we invoke an auxiliary "tilde" space $\tilde{\mathcal{H}}$, i.e., a copy of the original Hilbert space $\mathcal{H}$, such that for every state $|\varphi\rangle\in\mathcal{H}$ there is a copy $|\tilde{\varphi}\rangle\in\tilde{\mathcal{H}}$. For any density matrix $\rho(\boldsymbol{w})=\sum_j w_j|\varphi_j\rangle\langle\varphi_j|$, with fixed weights $\boldsymbol{w}=(w_1,w_2,\ldots)$, $|\varphi_j\rangle\in\mathcal{H}$ and $\langle\varphi_i|\varphi_j\rangle=\delta_{ij}$, there is a pure state $|\mathbf{0}(\boldsymbol{w})\rangle=\sum_j\sqrt{w_j}|\varphi_j\rangle\otimes|\tilde{\varphi}_j\rangle$. Thus, the expectation value of any physical operator $A:\mathcal{H}\to\mathcal{H}$ can be obtained as $\langle\mathbf{0}(\boldsymbol{w})|A|\mathbf{0}(\boldsymbol{w})\rangle=\sum_{jk}\sqrt{w_jw_k}\langle\varphi_j|A|\varphi_k\rangle\delta_{jk}=\mathrm{Tr}[A\rho(\boldsymbol{w})]$, and one recovers the original ensemble density by tracing out all the fictitious states: $\rho(\boldsymbol{w})=\mathrm{Tr}_{\tilde{\mathcal{H}}}[|\mathbf{0}(\boldsymbol{w})\rangle\langle\mathbf{0}(\boldsymbol{w})|]$ [70]. The field operators acting on the tilde space, i.e., the tilde fermionic operators $\tilde{c}_m$, $\tilde{c}_m^\dagger$, obey the same anticommutation rules as their untilde counterparts [43] and satisfy the anticommutation rules $\{c_m,\tilde{c}_m\}=\{c_m,\tilde{c}_m^\dagger\}=0$. By definition, operators acting on the physical space $\mathcal{H}$ do not act on states in the tilde space $\tilde{\mathcal{H}}$, and viceversa.

The weighted sum of the spectrum of a Hamiltonian $H=h+W$, with h and W being the free (noninteracting) and the interacting Hamiltonians, respectively, can be computed by resorting to the exponential parametrization of the configuration space [71]. To perform such a parametrization let us express the corresponding eigensystems as $H|\psi_j\rangle=E_j|\psi_j\rangle$ and $h|\psi_j^0\rangle=E_j^0|\psi_j^0\rangle$. It is well known that one may generate the states $\{|\psi_j\rangle\}$ by a unitary transformation of the set $\{|\psi_j^0\rangle\}$, as they constitute another orthonormal basis of the same Hilbert space [72]. Indeed, one can write $|\psi_j\rangle=\sum_k|\psi_k^0\rangle U_{kj}$, where the coefficients are the elements of a unitary matrix $\boldsymbol{U}$. As a consequence, the eigenstates can be represented in terms of an operator transformation: $|\psi_j\rangle=e^S|\psi_j^0\rangle$, where $S=\sum_{jk}S_{jk}|\psi_j^0\rangle\langle\psi_k^0|$ and S_{jk} is an anti-Hermitian matrix. Using the freedom for the definition of the replica states in Eq. (2) we fix $|\tilde{\psi}_j\rangle\equiv|\tilde{\psi}_j^0\rangle$, and obtain

$$|\mathbf{0}(\boldsymbol{w})\rangle=e^S|\mathbf{0}^0(\boldsymbol{w})\rangle, \tag{4}$$

where $|\mathbf{0}(\boldsymbol{w})\rangle=\sum_j\sqrt{w_j}|\psi_j\rangle\otimes|\tilde{\psi}_j^0\rangle$ is the *interacting* and

$$|\mathbf{0}^0(\boldsymbol{w})\rangle=\sum_j\sqrt{w_j}\,|\psi_j^0\rangle\otimes|\tilde{\psi}_j^0\rangle \tag{5}$$

is the *free* $\boldsymbol{w}$-field double states. We will write this latter state in terms of the single-particle states, as follows:

$$|\mathbf{0}^0(\boldsymbol{w})\rangle=\bigotimes_{m=1}^{L}(\sqrt{1-w_{s,m}}+\sqrt{w_{s,m}}c_m^\dagger\tilde{c}_m^\dagger)|\mathbf{0}\rangle, \tag{6}$$

where $\frac{1}{2}\geq w_{s,m}>0$ is the weight assigned to the *single* mode m, $|\mathbf{0}\rangle$ is the vacuum of the double space, and $\boldsymbol{w}$ denotes the many-mode weights $w_{n_1,\ldots,n_L}=\prod_{m=1}^{L}w_{s,m}^{n_m}(1-w_{s,m})^{1-n_m}$, with $n_m\in\{0,1\}$. A few comments are in order here. First, the state $|\mathbf{0}^0(\boldsymbol{w})\rangle$ resembles in form the superconducting state of Bardeen-Cooper-Schrieffer theory [73]—but here the "double" occupation is introduced for implementing the purification of mixed states rather than for describing a new phase of matter. Second, the distinctive state (6) can efficiently be prepared on a quantum computer [74], which highlights the potential and broad scope of our proposed method.

Further information on the noninteracting case is provided in Sec. I of the Supplemental Material (SM) [75] where, through the operator $G = \sum_m \theta_m (c_m^\dagger \tilde{c}_m^\dagger - \tilde{c}_m c_m)$, with $\cos(\theta_m) = \sqrt{1 - w_{s,m}}$, we get $|\mathbf{0}^0(\boldsymbol{w})\rangle = e^G|\mathbf{0}\rangle$ (the dependence of G on the weights being understood).

Going back to the interacting case, by multiplying (4) on the left by $e^G e^{-G}$ we get

$$|\mathbf{0}(\boldsymbol{w})\rangle = e^G e^{-G} e^S e^G |\mathbf{0}\rangle = e^G e^{S(\boldsymbol{w})}|\mathbf{0}\rangle. \tag{7}$$

Here, the short-hand notation $\mathcal{O}(\boldsymbol{w}) \equiv e^{-G}\mathcal{O}e^G$ applies. Thus, the state-average energy of the interacting system can be expressed as a pure state expectation value

$$\mathcal{E}(\boldsymbol{w}) = \langle \mathbf{0}(\boldsymbol{w})|H|\mathbf{0}(\boldsymbol{w})\rangle = \langle \mathbf{0}|e^{-S(\boldsymbol{w})}H(\boldsymbol{w})e^{S(\boldsymbol{w})}|\mathbf{0}\rangle.$$

As such, this formula resembles a single-reference calculation (in the double space) in which CC theories naturally arise [76]. This is the direction we take below.

Because the weights can be chosen in such a way that a Ritz-like variational principle for the underlying mixed states holds true [77–79], the state-average energy may thus be found by optimizing the anti-Hermitian matrix S_{jk} that *minimizes* $\langle \mathbf{0}|e^{-S(\boldsymbol{w})}H(\boldsymbol{w})e^{S(\boldsymbol{w})}|\mathbf{0}\rangle$, *as anticipated in Eq.* (3). Below, we give and validate an explicit form for S—please bear with us till then.

Thereafter, eigenstates can be obtained via straightforward projections: $|\psi_j\rangle \sim \langle \tilde{\psi}_j^0|\mathbf{0}(\boldsymbol{w})\rangle$. Unlike in approaches that use penalty terms to optimize the projection on *previously* determined states, in our approach eigenstates can be obtained *individually* or, in parallel, all at once. Given orthonormal single-particle orbitals to start with, formally, an optimization of a *single* pure (as opposed to a mixed) state is all that is required.

Eigenenergies and gaps without eigenstates.—Eigenenergies can be determined *without* having to reconstruct individual eigenstates. For this, let us express $\mathcal{E}(\boldsymbol{w})$ as the weighted sum of the contributions from each N-particle sector: $\mathcal{E}(\boldsymbol{w}) = \sum_N \mathcal{E}_N(\boldsymbol{w})$. Correspondingly, $|\mathbf{0}_\varphi(\boldsymbol{w})\rangle = \sum_N e^{iN\varphi}|\mathbf{0}_N(\boldsymbol{w})\rangle$, where

$$|\mathbf{0}_N(\boldsymbol{w})\rangle = \frac{1}{2\pi}\int_0^{2\pi} d\varphi\, e^{-iN\varphi}|\mathbf{0}_\varphi(\boldsymbol{w})\rangle. \tag{8}$$

The dependence of the state $|\mathbf{0}_\varphi(\boldsymbol{w})\rangle$ on the "angle" φ is detailed in Sec. I of the SM. As discussed in analogous contexts [80–86], Eq. (8) thus operates a projection with respect to a respective particle-number sector.

It is convenient to "normalize" the $\boldsymbol{w}$-field as follows: $|\mathbf{0}_N(\boldsymbol{w})\rangle \to |\mathbf{0}_N(\boldsymbol{w})\rangle/\sqrt{\mathcal{D}(\boldsymbol{w})}$, with $\mathcal{D}(\boldsymbol{w}) = (1 - w_{s,1})\cdots(1 - w_{s,L})$. As a result, the weighted sum of all the eigenenergies reads $\mathcal{E}_N(\boldsymbol{w}) = \sum_{\boldsymbol{n}} w_{n_1,\ldots,n_L} E_{n_1,\ldots,n_L}$, where $w_{n_1,\ldots,n_L} = \mu_1^{n_1}\cdots\mu_L^{n_L}$, with $\mu_m \equiv w_{s,m}/(1 - w_{s,m})$, $n_m \in \{0,1\}$ and $\sum_m n_m = N$. Next, $\boldsymbol{w}_i'$ stands for the tuple $\boldsymbol{w}$ where only the weight $w_{s,i} \to w_{s,i}'$ is changed. The energies of the N-particle sector can be extracted by the following rather simple prescription:

$$E_{n_{i_1},\ldots,n_{i_N}} = \frac{\Delta_{i_1}\cdots\Delta_{i_N}\mathcal{E}_N(\boldsymbol{w})}{\prod_{m=1}^N(\mu_{i_m} - \mu_{i_m}')}, \tag{9}$$

where $\Delta_i\mathcal{E}_N(\boldsymbol{w}) \equiv \mathcal{E}_N(\boldsymbol{w}) - \mathcal{E}_N(\boldsymbol{w}_i')$ [87]. In Eq. (9) only variational energies $\mathcal{E}(\boldsymbol{w})$ should be considered whose weight vectors $\boldsymbol{w}_s$, $\boldsymbol{w}_s'$ give rise to the *same* ordering of "collective" many-body indexes $j(\boldsymbol{n})$, as explained in Sec. II of the SM.

In the calculation of electron affinities g_+, ionization energies g_-, and fundamental gaps g, the original ground state is considered relative to the ground sates of the system with one more and one less particle. For which, we get

$$g_\pm = \sum_{p=0}^{1}(-1)^p\frac{\Delta_{i_1}\cdots\Delta_{i_{N\pm p}}\mathcal{E}_{N\pm p}(\boldsymbol{w})}{\prod_{m=1}^{N\pm p}(\mu_{i_m} - \mu_{i_m}')}, \tag{10}$$

and, thus, $g = g_- - g_+$.

Harnessing the framework.—Finally we exploit the above formalism by specifying $S(\boldsymbol{w})$ in terms of the UCC ansatz: $S = T - T^\dagger$, where T is the excitation operator defined according to $T = T_1 + T_2 + T_3 + \cdots$ [59]. Namely,

$$\begin{aligned} T_1 &= \sum_{mn} t_{mn} c_m^\dagger c_n, \\ T_2 &= \sum_{mnrs} t_{mnrs} c_m^\dagger c_n^\dagger c_r c_s, \end{aligned} \tag{11}$$

and higher-order terms follow the same structure where m, n, r, s index occupied or unoccupied orbitals. Thus, $S(\boldsymbol{w}) = T(\boldsymbol{w}) - T^\dagger(\boldsymbol{w})$.

Because of its high accuracy for ground-state calculations, the CC ansatz is sometimes referred to as the "gold standard of quantum chemistry" [71]. Although its "unitary" flavor is impractical on classical computers, it recently became clear that the UCC wave function can efficiently be handled on hybrid quantum-classical hardware like the variational eigensolvers [65,66]. One of the key ingredients of such an implementation is the exact identity for each of the different UCC factors appearing in the usual Trotter formula, i.e., $\exp[\vartheta_{i_1\cdots i_n}^{a_1\cdots a_n}(A_{i_1\cdots i_n}^{a_1\cdots a_n} - (A_{i_1\cdots i_n}^{a_1\cdots a_n})^\dagger)]$, where $\vartheta_{i_1\cdots i_n}^{a_1\cdots a_n}$ are variational parameters and $A_{i_1\cdots i_n}^{a_1\cdots a_n}$ are the excitation operators $c_{a_1}^\dagger\cdots c_{a_n}^\dagger c_{i_1}\cdots c_{i_n}$ [67,88–90]. We just need to operate the replacements $A_{i_1\cdots i_n}^{a_1\cdots a_n} \to A_{i_1\cdots i_n}^{a_1\cdots a_n}(\boldsymbol{w})$.

Validation.—Let us consider a 1D lattice model of spinless interacting fermions with Hamiltonian [91–93]

$$H = -\sum_{m=1}^{L}(c_m^\dagger c_{m+1} + c_{m+1}^\dagger c_m - U n_m n_{m+1}). \tag{12}$$

Here the operator $c_m^\dagger$ (c_m) creates (annihilates) a fermion on lattice site m, and U is the strength of the nearest-neighbor repulsion. For L sites, the Fock space can be decomposed in $L+1$ sectors: $\mathcal{F} = \mathcal{H}_0 \oplus \cdots \oplus \mathcal{H}_L$. Only L weights $w_{s,m}$ are needed in our prescription (one for each mode).

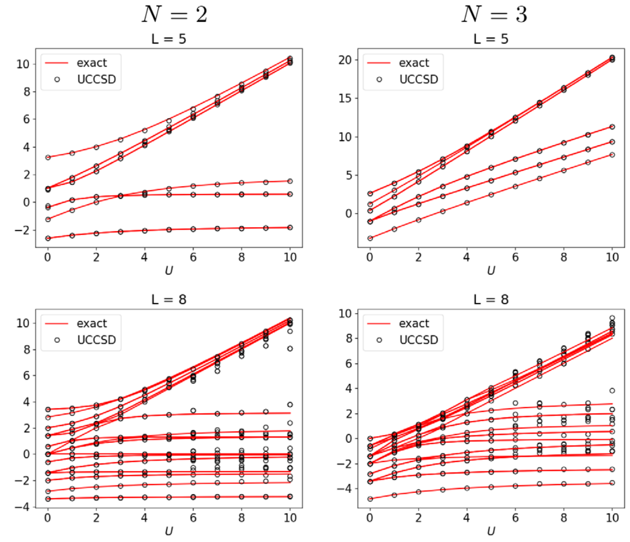

FIG. 1. The spectrum of the model (12) as a function of U for $N = 2, 3$ and $L = 5, 8$ sites. The red lines correspond to the exact energies. Single-particle weights $w_{s,m}$ were chosen decreasingly from 0.5 with spacing $-0.5/L$. For ease of comparison, for $L = 8$ we have plotted only the lowest 25 eigenenergies.

We implemented the factorized form of the UCC with singles and doubles (UCCSD). For the minimization of $\mathcal{E}(\boldsymbol{w})$ we have used the Nelder-Mead method with tolerance 10^{-5} [94]. Increasing the number of Trotter steps beyond 4 does *not* substantially improve our results presented below. Further details are reported in Sec. IV of the SM.

Let us compute the individual energies by extracting the states via the projection $|\psi_j\rangle \sim \langle\tilde{\psi}_j^0|\mathbf{0}(\boldsymbol{w})\rangle$ and compare them with the exact diagonalization results. In Fig. 1 we report the energies for $L \in \{5, 8\}$. For $L = 5$ our approach is near to be exact, due to reduced dimensionality of the corresponding Hilbert space. For $L = 8$, in the weakly correlation regime, the predicted energies are also in excellent agreement with the exact ones. Discrepancies become noticeable for $U \gtrsim 6$. The source of which are mainly: (a) UCCSD cannot handle strongly interacting states, most of all; (b) the increasing number of variational parameters for large L in the UCCSD ansatz (i.e., $\vartheta_{i_1 i_2}^{a_1 a_2}$) that must be determined in the minimization; and (c) the need of tighter tolerances in the minimization algorithm as a consequence of the increase of the Hilbert space's dimension. Moreover, because the weights are not variational, but fixed, auxiliary parameters, the results within a given approximations may be thus conditional on those values. Analytically, we find that $\mathcal{E}(\boldsymbol{w})$ can be written as $(1 - w_{s,m})\mathcal{A}_m(\boldsymbol{w}) + w_{s,m}\mathcal{B}_m(\boldsymbol{w})$, where $\mathcal{A}_m(\boldsymbol{w})$ and $\mathcal{B}_m(\boldsymbol{w})$ do not depend on $w_{s,m}$. This linearity, however, is observed as long as the *ordering* of the vector of many-body weights does not change. Interestingly, deviation from (*exact*) linearity may thus provide us with a way to sense the quality and stability of the results.

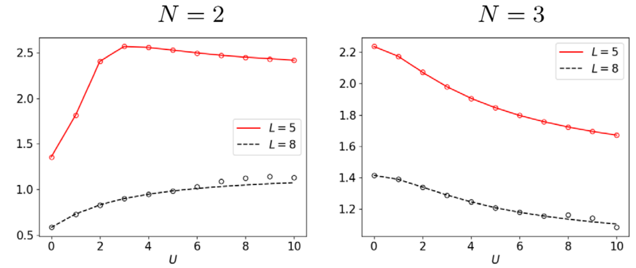

FIG. 2. Neutral gaps of the model (12) as a function of U for $N = 2$, 3 and $L = 5$, 8 sites. The solid and dashed lines correspond to the exact analytical gaps, while the red and black dots correspond to the energies computed with the energy-extraction method (9). We have employed weights as in Fig. 1 and $w'_{s,m} = w_{s,m} + 0.005$.

Finally, through Eq. (9)—i.e., *without* using any of the previously extracted eigenstates—we determine the energy gaps between the ground state and the lowest excited state of our model system for the same sectors of Fig. 1. The results shown in Fig. 2 with the exact result are, again, impressive.

Conclusions.—We have proposed a variational framework for determining the eigensystem of quantum many-body systems via the optimization of a *single* pure state. Such a pure state has the form of a *generalized* auxiliary thermofield, encoding excitations rather than thermodynamics. Which, we have shown, can be determined via the unitary couple cluster (UCC) approach. Because the UCC is suitable for an efficient implementation on quantum computers, our proposal may soon enable unprecedented calculations of excitations. But the framework we have built is general and, thus, it may be exploited to gain not only formal but also analytical and numerical advantages—in any type of variational methodology for excited states based on ensemble—yet to be explored.

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