Exactness of Two-Body Cluster Expansions in Many-Body Quantum Theory

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The Horn-Weinstein formula and the variational principle, combined with numerical results for a few many-electron systems, are used to provide support for a conjecture that the exact ground-state wave function for a Hamiltonian system containing up to two-body terms may be represented by an exponential cluster expansion employing a finite two-body operator.

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It has been suggested that it may be possible to represent the exact ground-state wave function of an arbitrary many-fermion pairwise interacting system by an exponential cluster expansion involving a general two-body operator [1–5]. If true, this could provide enormous reductions in computational requirements for accurate quantum calculations for many-fermion systems, eliminating the astronomical costs of generating the exact many-particle wave functions by solving the full configuration interaction (full CI) eigenvalue problem.

Specifically, it has been proposed that the exact ground-state wave function $|\Psi\rangle$ of a given many-fermion system described by the Hamiltonian containing up to two-body terms, obtained in a finite spin-orbital basis set, has the following simple form [1]:

$$|\Psi\rangle = e^X|\Phi\rangle, \tag{1}$$

where X is a general two-body operator and $|\Phi\rangle$ is a normalized reference state, which in principle is an arbitrary wave function that has a nonzero overlap with $|\Psi\rangle$, but in practice should reasonably well approximate $|\Psi\rangle$. In the language of second quantization,

$$X = \tfrac{1}{2}x^{rs}_{pq}c^p c^q c_s c_r, \tag{2}$$

where c^p (c_p) are the usual creation (annihilation) operators ($c^p = c_p^\dagger$) associated with a given orthonormal spin-orbital basis set, x^{rs}_{pq} are some coefficients, and the Einstein summation convention is assumed. According to Nooijen [1], the number of independent coefficients x^{rs}_{pq} should be identical to the number of two-particle integrals v^{rs}_{pq} that enter the Hamiltonian:

$$H = z^q_p c^p c_q + \tfrac{1}{2}v^{rs}_{pq}c^p c^q c_s c_r. \tag{3}$$

One could redefine X by considering the one- and two-body components in Eq. (2) [2,3], but this is not really necessary since, for a fixed number of particles (N), one can always rewrite H in terms of two-body terms only:

$$H = \tfrac{1}{2}h^{rs}_{pq}c^p c^q c_s c_r, \tag{4}$$

where $h^{rs}_{pq} = v^{rs}_{pq} + (z^r_p\delta^s_q + \delta^r_p z^s_q)/(N-1)$, with δ^q_p representing the usual Kronecker delta.

Of all arguments in favor of the correctness of Eq. (1) given in the earlier papers on this topic [1–5], the most convincing is the recent calculation performed by Van Voorhis and Head-Gordon, who attempted to minimize the expectation value expression,

$$E(\tilde{X}) = \langle\Phi|e^{\tilde{X}^\dagger}He^{\tilde{X}}|\Phi\rangle/\langle\Phi|e^{\tilde{X}^\dagger}e^{\tilde{X}}|\Phi\rangle, \tag{5}$$

over two-body operators,

$$\tilde{X} = \tfrac{1}{2}\tilde{x}^{rs}_{pq}c^p c^q c_s c_r, \tag{6}$$

obtaining quite accurate energies for a few small many-electron systems [5]. The only problem is that these authors did not use the exact form of the wave function, Eq. (1), but, rather, a truncated power series in X corresponding to Eq. (1). In addition, the 6-electron/12-spin-orbital STO-3G model of the nitrogen molecule, studied in Ref. [5], is so small that the number of independent parameters x^{rs}_{pq} is larger than the dimension of the corresponding N-electron Hilbert space (the full CI eigenvalue problem). With an exception of very small systems and small basis sets, the number of two-body parameters is considerably smaller than the dimension of the full CI problem, so one has to test Eq. (1) on other systems.

This Letter provides strong evidence that the exact ground state of a many-fermion system, described by the Hamiltonian containing one- and two-body terms, may indeed be represented by the exponential cluster expansion employing a general two-body operator by connecting the problem with the Horn-Weinstein formula [6],

$$\begin{aligned} E &= \lim_{t\to\infty}\langle\Phi|e^{-tH}H|\Phi\rangle/\langle\Phi|e^{-tH}|\Phi\rangle = \lim_{t\to\infty}E_t \\ &= \lim_{t\to\infty}E(X_t), \end{aligned} \tag{7}$$

where E is the exact ground-state energy,

$$E_t \equiv E(X_t) = \langle\Phi|e^{X_t^\dagger}He^{X_t}|\Phi\rangle/\langle\Phi|e^{X_t^\dagger}e^{X_t}|\Phi\rangle, \tag{8}$$

and

$$X_t = -\tfrac{1}{2}tH, \tag{9}$$

and by determining the operator X entering Eq. (1)

through a direct minimization of the exact form of the expectation value expression $E(\tilde{X})$, Eq. (5), over two-body operators $\tilde{X}$, Eq. (6), for a few many-electron systems. Let us recall that the Horn-Weinstein formula, Eq. (7), provides a basis of the t-expansion method [6], which allows one to extract the exact properties of physical systems by considering the Padé approximants for the power series in t representing E_t or dE_t/dt [6–8]. Other variants of the t-expansion method, combining the original approach of Ref. [6] with the real-space renormalization group and path integral techniques, have been proposed in Refs. [9,10]. The t-expansion method has been applied to spin systems [6], non-Abelian lattice gauge theories [7,8,11], and the Lipkin model [12], and to formulate the connected-moment energy expansions [13,14]. The results obtained by minimizing the energy expression $E(\tilde{X})$, Eq. (5), over two-body operators $\tilde{X}$ are compared in this Letter with the ground-state energies of a few many-electron systems obtained with the t-expansion method.

Let us begin with the formal arguments, which indicate that the existence of a two-body operator X, defined by finite coefficients x_{pq}^{rs}, producing the exact ground state $|\Psi\rangle$ according to Eq. (1), might be a real possibility. Consider the family $\mathcal{M}$ of all two-body operators $\tilde{X}$, Eq. (6), that are defined by finite coefficients $\tilde{x}_{pq}^{rs}$ and that have a general structure of the Hamiltonian H, Eq. (4). This means that $\mathcal{M}$ consists of all two-body operators that are, for example, Hermitian, since H is Hermitian, and that satisfy relations, such as $\tilde{x}_{pq}^{rs} = \tilde{x}_{qp}^{sr}$, since $h_{pq}^{rs} = h_{qp}^{sr}$. Obviously, the number of independent parameters $\tilde{x}_{pq}^{rs}$ is identical to the number of coefficients h_{pq}^{rs} or v_{pq}^{rs} defining the Hamiltonian. It should be noticed that all operators X_t, Eq. (9), belong to $\mathcal{M}$, although $\mathcal{M}$ is a much larger operator family, which contains infinitely many operators that are not multiples of H. This remark is important here, since one can always obtain the exact wave function by considering the expression (exploited in Quantum Monte Carlo calculations)

$$|\Psi\rangle = \lim_{t\to\infty} e^{Z_t}|\Phi\rangle, \tag{10}$$

where $Z_t \in \mathcal{M}$ is defined as

$$Z_t = -(H - E)t. \tag{11}$$

The main difference between Eqs. (1) and (10) is in the fact that X, Eq. (2), is a finite two-body operator which, as we show below, is not of the Hamiltonian form, whereas Z_t, Eq. (11), and X_t, Eq. (9), are multiples of the Hamiltonian. Thus, the Z_t and X_t operators can provide the exact energy and wave function *only in the* $t \to \infty$ *limit* [the t-dependent energy E_t, Eq. (8), is a monotonically decreasing function of t, which approaches the exact ground-state energy E from above [6]]. This implies that, in looking for the operator X defining $|\Psi\rangle$ through Eq. (1), we cannot constrain X to be of the Hamiltonian form.

Let us, therefore, minimize $E(\tilde{X})$, Eq. (5), over all operators in $\mathcal{M}$. According to the variational principle, $E(\tilde{X})$ is bounded from below, $E \le E(\tilde{X})$ for all operators $\tilde{X} \in \mathcal{M}$, which implies that there should exist a two-body operator $X \in \mathcal{M}$ that minimizes $E(\tilde{X})$,

$$E(X) = \min_{\tilde{X}\in\mathcal{M}} E(\tilde{X}). \tag{12}$$

Clearly,

$$E \le E(X). \tag{13}$$

Consider the energy expression E_t, Eq. (8), for an arbitrary (fixed) value of t. We can write

$$E(X) < E_t. \tag{14}$$

Equation (14) is valid, since $E(X)$ is a minimum value of $E(\tilde{X})$, Eq. (5), in a space of all two-body operators $\tilde{X}$, whereas $E_t = E(X_t)$ is the value of $E(\tilde{X})$ at $\tilde{X} = X_t$ [cf. Eqs. (5) and (8)]. In fact, for a given value of t, one can always easily find a two-body operator Y from $\mathcal{M}$ such that $E(Y) < E_t$. An example of such an operator might be $X_{t'}$ with $t' > t$, since E_t, Eq. (8), is a monotonically decreasing function of t [6]. However, since the operator family $\mathcal{M}$ is much larger than the "one-dimensional" manifold of operators X_t, which are multiples of H, there may exist two-body operators $Y \in \mathcal{M}$ which satisfy $E(Y) < E_t$ and which are not given by Eq. (9). This indicates that the operator X minimizing $E(\tilde{X})$ may very well be a finite operator (i.e., defined by finite coefficients x_{pq}^{rs} and not obtained by considering the limiting case of the $t \to \infty$ operators X_t), although we cannot provide a rigorous mathematical proof that this is indeed the case. The existence of a finite operator $X \in \mathcal{M}$ that minimizes $E(\tilde{X})$ according to Eq. (12) and that is not of the Hamiltonian form is supported in this Letter by the numerical calculations for a few many-electron systems.

Once X is determined by minimizing $E(\tilde{X})$, the inequalities (13) and (14) can be combined into

$$E \le E(X) < E_t, \tag{15}$$

true for any value of t. In view of Eq. (7), by considering the $t \to \infty$ limit in Eq. (15), we immediately obtain

$$E = E(X), \tag{16}$$

so that the two-body operator X, minimizing $E(\tilde{X})$, gives the exact energy E and, in view of the variational principle, the exact ground state $|\Psi\rangle$, as stated in Eq. (1).

Although the above analysis cannot be regarded as the complete mathematical proof of Eq. (1), since we cannot rigorously prove the existence of the finite coefficients x_{pq}^{rs} that would define the optimum operator X, the advantage of the above reasoning over the arguments given in Refs. [3,5] is that it frees us from necessarily assuming that operator X is obtained by studying the $t \to \infty$ operators X_t, Eq. (9), or Z_t, Eq. (11). By minimizing $E(\tilde{X})$, Eq. (5), in the space of all two-body

operators [or, equivalently, by minimizing $E(\tilde{X})$ in a finite-dimensional space of variables $\tilde{x}^{rs}_{pq}$], which is exactly how we obtain operator X, we may be able to find finite parameters x^{rs}_{pq}, defining the exact wave function $|\Psi\rangle$, because the *operator X is not constrained to be a multiple of H*. If the finite operator X, found by some numerical procedure for minimizing $E(\tilde{X})$, is a local rather than a global minimum on the $E(\tilde{X})$ multiparameter surface, then the resulting energy and wave function do not have to be exact. However, even in this case, the operator X may provide excellent results, opening thus a possibility of using wave functions (1) in high-accuracy *ab initio* calculations.

We have, in fact, numerical evidence that supports the above statements. For example, by minimizing $E(\tilde{X})$ for a 6-electron/12-spin-orbital STO-3G model of the nitrogen molecule, described in Ref. [5], at the equilibrium geometry (the N–N distance of 2.068 bohrs), we obtained the energy of $-107.619\,941\,82$ hartrees, which is precisely the exact, full CI, energy (to within 10^{-8} hartrees). For an overlap of the normalized wave function $|\Psi\rangle$, Eq. (1), generated with the optimum operator X, and the normalized full CI wave function, we obtained 1.000 000, which should be compared to an overlap of 0.962 583 between the normalized full CI wave function and reference $|\Phi\rangle$ [we used the restricted Hartree-Fock wave function as $|\Phi\rangle$]. Although in this case the number of independent parameters x^{rs}_{pq} is larger than the dimension of the corresponding N-electron Hilbert space, so that the exactness of Eq. (1) might be regarded as rather obvious, the absolute values of the coefficients x^{rs}_{pq}, defining the optimum operator X, are small (ranging between 0.000 073 and 0.202 417). More importantly, the optimum coefficients x^{rs}_{pq} do not satisfy the relations $x^{rs}_{pq} = -\frac{1}{2}t\,h^{rs}_{pq}$ or $x^{rs}_{pq} = -t(h^{rs}_{pq} - \epsilon\,\delta^r_p\delta^s_q)$, implied by Eqs. (9) and (11) (ϵ is a constant shift), and $[X, H] \neq 0$, so that X is not of the Hamiltonian form. *We must emphasize that in this and other test cases described below, we tested (for the first time ever) the exact theory, in which we used the unexpanded form of $e^{\tilde{X}}$ to define $E(\tilde{X})$ rather than the truncated power series expansion in $\tilde{X}$ used in Ref.* [5]. This was made possible by representing H and $\tilde{X}$ as matrices in the corresponding finite-dimensional N-electron Hilbert spaces (using all Slater determinants $|\Phi_\lambda\rangle$ defining the full CI problem as basis states). In order to calculate the exact value of $E(\tilde{X})$, Eq. (5), in a given iteration of the procedure used to minimize $E(\tilde{X})$, we first diagonalized the matrix representing $\tilde{X}$ with some unitary matrix $\tilde{U}$ to obtain the diagonal matrix $\tilde{D} = \tilde{U}\tilde{X}\tilde{U}^{-1}$. Next, we constructed $e^{\tilde{D}}$ by taking the exponentials of the diagonal elements of $\tilde{D}$. After constructing $e^{\tilde{D}}$, we calculated the matrix representing $e^{\tilde{X}}$ as $\tilde{U}^{-1}e^{\tilde{D}}\tilde{U}$ and applied it to a column vector representing $|\Phi\rangle$ to obtain $|\Psi\rangle$, Eq. (1). The value of $E(\tilde{X})$ was obtained as $\langle\Psi|H|\Psi\rangle/\langle\Psi|\Psi\rangle$, using matrices representing H and $|\Psi\rangle$. We minimized $E(\tilde{X})$ in $\mathcal{M}$ by the following methods: the downhill simplex method, the continuous minimization by simulated annealing, and the conjugate gradient method [15]. The calculations for N_2 required $\sim$50 iterations to obtain the convergence. The calculations for other many-electron systems described below required a hundred or so iterations to obtain a reasonably converged result. Clearly, our numerical procedures are not suitable for larger problems. The point of this paper is the possibility of representing the (virtually) exact many-fermion wave functions by Eq. (1) and the evidence that supports such a claim.

Our findings for N_2 apply to other many-electron systems, including the 4-electron/8-spin-orbital H_4 clusters [16] and the 8-electron/16-spin-orbital H8 model [17] (eight hydrogen atoms arranged in a distorted octagonal configuration). The example of the H8 system is particularly important, since in this case the number of two-body parameters x^{rs}_{pq}, used in our calculations, or the number of independent two-body integrals h^{rs}_{pq}, defining the Hamiltonian (186), are considerably smaller than the number of all spin- and symmetry-adapted configurations defining the full CI problem (468). For the $\alpha = 1.0$ H8 model (α is the parameter of this model, in bohrs, that describes the deviation of the geometry of the H8 system from the regular octagon [17]), we have already lowered $E(\tilde{X})$ to $-4.352\,982$ hartrees. This result agrees with the exact, full CI, energy to within 8×10^{-6} hartrees. The overlap of the normalized wave function $|\Psi\rangle$, Eq. (1), obtained by minimizing $E(\tilde{X})$, with the normalized full CI wave function $|\Psi^{\mathrm{FCI}}\rangle$ is in this case 0.999 998 (compared to $|\langle\Phi|\Psi^{\mathrm{FCI}}\rangle| = 0.939\,657$). For a demanding $\alpha = 0.0001$ H8 model, characterized by a strong configurational quasidegeneracy [17], we obtained an agreement with the exact, full CI, energy to within 5.2×10^{-5} hartrees and an overlap of the normalized wave function $|\Psi\rangle$, Eq. (1), with $|\Psi^{\mathrm{FCI}}\rangle$ of 0.999 987 (compared to $|\langle\Phi|\Psi^{\mathrm{FCI}}\rangle| = 0.668\,268$). This is very encouraging, since, for example, the standard two-body coupled-cluster theories [18,19], including coupled-cluster doubles and coupled-cluster singles and doubles, which use the exponential form of the wave function $e^T|\Phi\rangle$, where T is the excitation operator, give the 6.030 and 5.034 millihartree errors, respectively, in this case. In both cases of the $\alpha = 1.0$ and $\alpha = 0.0001$ H8 models, the resulting parameters x^{rs}_{pq} have small absolute values (at most 0.316 845 for $\alpha = 1.0$ and at most 0.596 623 for $\alpha = 0.0001$) and $[X, H] \neq 0$. It is, thus, possible that the two-body operator X, describing the exact wave function via Eq. (1), is defined by finite, relatively small, coefficients x^{rs}_{pq}, which can be obtained by minimizing $E(\tilde{X})$. Even if our numerical procedures do not produce the exact (in a mathematical sense) energies, but, rather, some local minima of $E(\tilde{X})$, the very small errors on the order of 10^{-5}–10^{-6} hartrees, obtained with two-body operators only, are intriguing.

Finally, let us compare the energies $E(X)$, obtained by minimizing $E(\tilde{X})$, for a nontrivial many-electron system, such as H8, where the number of parameters x^{rs}_{pq}

is significantly smaller than the dimension of the corresponding N-electron Hilbert space, with the results of calculations employing the Padé approximants for E_t, Eq. (8), or dE_t/dt, as explained and exploited by Horn and Weinstein [6–11]. The Padé approximants for E_t or dE_t/dt can be used to extract the virtually exact energies of quantum many-body systems corresponding to the $t \rightarrow \infty$ limit of E_t, Eq. (7) [6–11]. Thus, it is useful to examine if the direct minimization of $E(\tilde{X})$, Eq. (5), provides better energies than those obtained by forming the Padé approximants for E_t or dE_t/dt. As explained in Ref. [6], in the case of using dE_t/dt, one calculates the energy by integrating the $[L, L']$ Padé approximant for dE_t/dt with $L' - L \geq 2$ over t from 0 to $t_{\max}$, where $t_{\max}$ is the largest value of t for which this Padé approximant remains negative (in theory, $dE_t/dt < 0$ for all values of t [6]). In our calculations for the H8 system, we calculated the Padé approximants for E_t and dE_t/dt by considering the power series expansions of E_t to order t^{11}. Thus, we had access to all Padé approximants with $L + L' \leq 11$ (for E_t) or $L + L' \leq 10$ (for dE_t/dt).

Our findings for the $\alpha = 1.0$ and $\alpha = 0.0001$ H8 systems are as follows: The Padé approximant extrapolations for E_t give a slow convergence with L and L'. The resulting energies are rather poor. For example, of all diagonal approximants for E_t that we could calculate from our data, the best results were obtained with the [4,4] and [5,5] approximants. For the $\alpha = 1.0$ H8 model, the [4,4] approximant gave the energy of $-4.343\,813$ hartrees. This should be compared with the exact, full CI, energy of $-4.352\,990$ hartrees and with the $E(X)$ value of $-4.352\,982$ hartrees. For the $\alpha = 0.0001$ H8 model, the [5,5] approximant gave the energy of $-4.205\,334$ hartrees, which should be compared with the exact energy of $-4.204\,803$ hartrees and $E(X) = -4.204\,751$ hartrees. Our $E(X)$ values, obtained by minimizing $E(\tilde{X})$, are considerably better. The Padé approximant extrapolations for dE_t/dt, followed by integrations over t, turned out to be more reliable, particularly for the $\alpha = 1.0$ H8 system. However, even in this case, our $E(X)$ values are better. Of all integrable approximants for dE_t/dt that we could form from our data, the best results for the $\alpha = 1.0$ H8 model were obtained with the [0,8], [1,9], and [0,9] approximants. These three approximants gave the energies of $-4.352\,962$, $-4.352\,953$, and $-4.352\,940$ hartrees, respectively, or the 2.8×10^{-5}, 3.7×10^{-5}, and 5.0×10^{-5} hartree differences with the exact energy. This should be compared with the 8×10^{-6} hartree difference between $E(X)$ and the full CI energy. The best result for the $\alpha = 0.0001$ H8 model was obtained with the [4,6] approximant, which gave the energy of $-4.205\,128$ hartrees or the -3.25×10^{-4} hartree difference with the exact energy. This should be compared with the smaller, 5.2×10^{-5} hartree, difference between $E(X)$ and the full CI energy. In the case of the $\alpha = 0.0001$ H8 model, many Padé approximants for dE_t/dt have singularities in the region of the negative values of dE_t/dt, making them unusable in the energy calculations. No such problems occur in the direct minimization of $E(\tilde{X})$.

In summary, by combining the theoretical arguments based on the Horn-Weinstein formula with the variational principle and numerical calculations, we demonstrated that one can obtain the virtually exact description of pairwise interacting many-fermion systems by representing their wave functions by exponential cluster expansions employing two-body operators. The two-body operators defining these cluster expansions are finite and not of the Hamiltonian form. A direct minimization of the energy expression involving the two-body operator defining the many-particle wave function leads to the results that are better than those obtained with the Padé approximants of the time-dependent energies defining the Horn-Weinstein expression for the exact energy.

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