Exactness of the General Two-Body Cluster Expansion in Many-Body Quantum Theory

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We show that the exact ground-state wave function for an arbitrary two-body Hamiltonian in second-quantized, finite basis set, form cannot generally be represented by a generalized coupled-cluster operator with real finite matrix elements acting on an arbitrary initial trial function.

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Recently it has been suggested that it may be possible to represent the exact ground-state wave function of an arbitrary many-fermion system with only pairwise forces by an exponential cluster expansion involving a general two-body operator [1–5]. This speculation has been supported by numerical examples that are exact within the limits of the computations reported. Here we will show that this result cannot generally be true.

Specifically, if we consider the representation of all operators in a finite basis of dimension r for a system with N electrons, the general Hamiltonian involving only zero- (i.e., constant), one-, and two-body operators symmetric in the particles may always be written in terms of annihilation and creation operators as

$$H = \sum h_{pq}^{rs} a_p^\dagger a_q^\dagger a_s a_r. \quad (1)$$

For an H of interest in electronic structure calculations, the operator is real, Hermitian, symmetric in the particles, and independent of spin. The proposition is then that the exact ground-state wave function for this second-quantized Hamiltonian may be written as

$$(H - E)\Psi = 0, \qquad \Psi = \exp(W)\Phi, \quad (2)$$

where W has the same form as H

$$W = \sum w_{pq}^{rs} a_p^\dagger a_q^\dagger a_s a_r, \quad (3)$$

and Φ is an arbitrary initial guess not orthogonal to Ψ. Here we will be considering the realistic case where $r - N \gg N \gg 4$ so that it requires of the order of r^N coefficients to specify Ψ as a linear combination of configurations while H and W both contain only of the order of r^4 parameters. In all examples in the literature the matrix elements in W have been constrained to be real and we will make that assumption here. Therefore $\exp(W)$ can approach zero only if some matrix elements defining W become infinite.

As is well known, there is at least one example of a W of the form of Eq. (3), namely

$$W = \lim_{t\to\infty}(-tH). \quad (4)$$

Further, W is not unique if Ψ and Φ are both eigenfunctions of zero-, one-, or two-body operators that commute with H. Such operators often include the unit operator $\mathbf{1}$, the total spin in the z direction S_z, the square of the total spin S^2, and the sum P_2 of all pairwise permutations.

Hence, if W works, so does $W - a\,\mathbf{1} - b\,S_z - c\,S^2 - d\,P_2$. In the numerical examples in the literature the authors were able to find a W with real finite matrix elements that gave extremely accurate results, so we will consider that case here. If W has only real finite elements, then $\exp(-W)$ is the inverse of $\exp(W)$. Since a W with finite matrix elements differs from Eq. (4), the literature implicitly assumes that W is nonunique in ways other than the one mentioned here.

It is easy to find an example where a different choice of W can be shown to be exact. The Hamiltonian defined as

$$H = \sum_{i=1}^{N/2} h_i^{i+N/2}(q_i^{i+N/2} + q_{i+N/2}^{i}),$$
$$q_i^j = a_{j\alpha}^\dagger a_{j\beta}^\dagger a_{i\beta} a_{i\alpha}, \quad (5)$$

involving only disjoint double replacements has an eigenfunction

$$\Psi = \exp(W)\Phi, \qquad \Phi = a_{N/2\alpha}^\dagger a_{N/2\beta\ldots}^\dagger a_{1\alpha}^\dagger a_{1\beta}^\dagger|0\rangle,$$
$$W = \sum_{i=1}^{N/2} q_i^{i+N/2}, \quad (6)$$

which is of the usual coupled-cluster (CC) doubles form. Here α and β label the spin of the orbitals. Notice this W is independent of the h_i^j matrix elements and will be the ground state if all h_i^j are negative. Piecuch *et al.* [5] had suggested that W should be restricted to be Hermitian and of the same form and symmetry as H in agreement with Eq. (4), but W in this example, like the usual CC operator, is not Hermitian. Also it should be noted that W used by Voorhis and Head-Gordon [4] was not Hermitian. Nevertheless, both Voorhis and Head-Gordon and Piecuch *et al.* obtained results that were exact to within numerical accuracy.

Another example where W is known to exist is if H is actually a one-body operator written in two-body form.

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In this case its eigenfunction, Ψ_1, can be chosen to be a Slater determinant. Thouless [6] showed that any Slater determinant Ψ_1 can be derived from any other one Φ_1 by a transformation of the form $\exp(W)\Phi_1$ where W is also only a one-body operator. We may [7] choose W to be skew symmetric so that $\exp(W)$ is unitary. Notice Φ_1 must be the eigenfunction of some other operator H_1 given by $\exp(-W)H\exp(W)$. Expansion of this form for H_1 in a power series in W is easily shown to involve only one-body operators because commutators of one-body operators are still one-body operators. Hence H_1 will also be a Hermitian one-body operator which is consistent with the assumed single Slater determinant form for Φ_1. For the general two-body case, Φ must also be the eigenfunction of H_2 given by $\exp(-W)\ H\exp(W)$ if W is finite, but in this case H_2 will be an N-body non-Hermitian operator for almost all H and W. Hence the one-body case is very different from the two-body case.

As Piecuch *et al.* noted [5], the choice of $-\alpha H$ for W gives an average energy that is monotonic decreasing as a function of increasing α and has no minimum for any finite α. In fact, no expression of the form $f(H)\Phi$ can generally be exact if $f(H)$ has an inverse because f and H will commute and

$$
\begin{aligned}
Hf(H)\Phi &= Ef(H)\Phi, \\
f(H)^{-1}Hf(H)\Phi &= H\Phi = E\Phi.
\end{aligned} \tag{7}
$$

Hence Φ must already be an eigenfunction of H. This contradicts one example given by Nakatsuji [2] and suggests that his result was not fully optimized.

In the following equations we will follow Nooijen [3] and abbreviate the general two-body operators in the equation for H or W as q_μ. In Nakatsuji's original paper [1] on the structure of the exact wave function he noted that a necessary and sufficient condition for a wave function to be exact is that

$$\langle\Psi|q_\mu(H-E)|\Psi\rangle = 0 \tag{8}$$

for all q_μ. The necessity is obvious and the sufficiency follows because one weighted sum of these equations gives

$$\langle\Psi|H(H-E)|\Psi\rangle = 0, \tag{9}$$

while another sum gives

$$\langle\Psi|\mathbf{1}(H-E)|\Psi\rangle = 0. \tag{10}$$

Combining these gives

$$\langle\Psi|(H-E)^2|\Psi\rangle = 0, \tag{11}$$

which can only be satisfied by an exact eigenfunction of H. Nakatsuji [1] then examined the condition for W to give a minimum average energy and arrived at another equation that can be written in the form

$$\langle\Psi|\{q_\mu + 1/2[q_\mu, W] + 1/6[[q_\mu, W], W]\ldots\} \times (H-E)|\Psi\rangle = 0. \tag{12}$$

Since this differs from Eq. (8) he concluded that Ψ will not in general be exact. Actually this is not conclusive since $(H-E)\Psi$ would be 0 for an exact Ψ, so Ψ would satisfy both equations if it were exact. In fact in later papers he used this exponential form to obtain numerically precise results [2].

As Nooijen noted [3], the number of Eqs. (8) to be satisfied is equal to the number of parameters in W. Hence if the equations are solvable with finite matrix elements w_μ, then an exact wave function of the form $\exp(W)\Phi$ would exist and would be computable. It is tempting to believe that the set of all H of the form (1) define a set of permissible ground-state wave functions smaller than the full vector spanned by all N-body configurations that can be formed from r orbitals. Strangely this is not true because this form for H includes the unit operator for which every vector is an eigenvector. Much information about the original form of the Schrödinger operator is lost in passing to second-quantized form with a finite basis set. Hence the claim that $\exp(W)\Phi$ can be exact for every H of the form (1) and every trial Φ is equivalent to claiming that

$$\Psi = \exp(W)\Phi \tag{13}$$

has a solution for every Φ and Ψ. Now the same argument about dimensionality that led to the hypothesis that W existed works against it. The vectors Φ and Ψ can be two arbitrary vectors and (13) represents a set of $\sim r^N$ equations in $\sim r^4$ variables with N and $r-N$ generally much larger than 4. Hence there will generally not be a solution. In fact, for a given H with a nondegenerate ground state, Ψ will be fixed. The vector Φ will then need to lie in the set defined by

$$\Phi = \exp(-W)\Psi \tag{14}$$

as the elements w_μ are varied. If the elements of W are constrained to lie in some bounded region $|w_\mu| < R$, this set of Φ will not include all vectors. The set of possible Φ do not form a linear vector space since $\exp(-W_1) + \exp(-W_2)$ cannot usually be rewritten as $\exp(-W)$. Except for a set of measure zero out of the set of all Ψ, the set of all Φ related to Ψ will not include single Slater determinants or any other arbitrarily selected initial form for the wave function. If it happens that a particular pair Φ, Ψ are related by some W with finite matrix elements as in Eq. (6), then W is specific to this pair unlike W in Eq. (4) which is independent of Φ. Thus in the example of Eq. (6), if Φ were replaced by $\exp(T)\Phi$ as the trial function (where T is a general two-body operator) generally no two-body operator X would exist so that $\exp(X)\{\exp(T)\Phi\}$ would be Ψ. This would require that $\exp(X) = \exp(W)\exp(-T)$, where all three operators are of two-body form.

Hence the conclusion is that a W with bounded real matrix elements usually does not exist that would turn an arbitrary Φ into an exact eigenfunction of an arbitrary H of the form (1). The assumption that such a W exists implies the existence of $\exp(-W)$ as the inverse of $\exp(W)$. This contrasts with Eq. (4) which has an unbounded W so that $\exp(W)$ is a projection operator and has no inverse.

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[1] H. Nakatsuji, J. Chem. Phys. **113**, 2949 (2000).
[2] H. Nakatsuji, J. Chem. Phys. **115**, 2465 (2001).
[3] M. Nooijen, Phys. Rev. Lett. **84**, 2108 (2000).
[4] T.V. Voorhis and M. Head-Gordon, J. Chem. Phys. **115**, 5033 (2001).
[5] P. Piecuch, K. Kowalski, P.-D. Fan, and K. Jedziniak, Phys. Rev. Lett. **90**, 113001 (2003).
[6] D. J. Thouless, Nucl. Phys. **21**, 225 (1960).
[7] E. Dalgaard and P. Jorgensen, J. Chem Phys. **64**, 3833 (1978).