# Can the Eigenstates of a Many-Body Hamiltonian Be Represented Exactly Using a General Two-Body Cluster Expansion?

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Using a general two-body exponential parametrization for the wave function, the Nakatsuji two-particle density equation [Phys. Rev. A **14**, 41 (1976)] is transformed into a set of nonlinear algebraic equations in which the number of unknowns precisely equals the number of equations. Since the Nakatsuji two-particle density equation is equivalent to the time-independent Schrödinger equation for Hamiltonians containing up to two-body interactions, the answer to the title question is affirmative, *provided the equations have solutions*. Practical implications of the parametrization and possible approximation schemes are briefly discussed.

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In 1976, Nakatsuji [1] derived a hierarchy of so-called density equations and showed that an electronic wave function that satisfies the two-particle density equation necessarily satisfies the time-independent electronic Schrödinger equation. The density equation does not require the wave function but instead allows a formulation in terms of reduced density matrices (RDMs) directly. This introduces the infamous $N$-representability problem, however: The density equation has to be solved under the constraints that the RDMs correspond to a wave function that has the proper symmetry properties, e.g., that it be antisymmetric for fermions (see, e.g., [2]). Valdemoro has pioneered the use of the density equation, also called the contracted Schrödinger equation (for recent reviews, see [3,4]), and very recently the use of the density equation has been explored further, yielding promising results (e.g., [5,6]).

Instead of using the density matrix formulation, we attempt to solve the density equation employing a suitable parametrization for the wave function, and hence the $N$-representability problem does not arise. The number of nonlinear parameters in the wave function is equal to the dimension of the two-particle Nakatsuji density equation, and the parametrization is exact, *provided* the equations have a solution.

We focus on the case of the electronic Schrödinger problem and use a finite dimensional many-electron basis defined by a finite set of one-electron spin orbitals. The Hamiltonian is expressed in second quantization as

$$\hat{H} = h^q_p \hat{a}^p_q + \tfrac{1}{4} V^{pq}_{rs} \hat{a}^{rs}_{pq}\,, \tag{1}$$

where $V^{pq}_{rs}$ indicates antisymmetrized two-electron integrals and the operators are defined as

$$\hat{a}^p_q = \hat{a}^\dagger_p \hat{a}_q, \qquad \hat{a}^{pq}_{rs} = \hat{a}^\dagger_p \hat{a}^\dagger_q \hat{a}_s \hat{a}_r, \ldots \tag{2}$$

and the Einstein summation convention is used. The annihilation and creation operators satisfy the usual anticommutation relations. Nakatsuji showed more than 20 years ago that if the so-called $n$-particle density equation is satisfied for a Hermitian Hamiltonian containing at most $n$-particle interactions, the wave function is necessarily an exact eigenstate of the Hamiltonian. The proof is simple and elegant. It uses the fact that a normalized state $|\Psi\rangle$ is an exact eigenstate if and only if

$$\langle\Psi|\hat{H}^2|\Psi\rangle = \langle\Psi|\hat{H}|\Psi\rangle^2 \equiv E^2. \tag{3}$$

Substituting the second quantized expression for the two-body Hamiltonian operator [Eq. (1)] one obtains

$$h^q_p \langle\Psi|\hat{a}^p_q \hat{H}|\Psi\rangle + \tfrac{1}{4} V^{rs}_{pq} \langle\Psi|\hat{a}^{pq}_{rs} \hat{H}|\Psi\rangle = h^q_p \langle\Psi|\hat{a}^p_q|\Psi\rangle E + \tfrac{1}{4} V^{rs}_{pq} \langle\Psi|\hat{a}^{pq}_{rs}|\Psi\rangle E\,. \tag{4}$$

Therefore the normalized wave function is exact (within the limitations of the finite one-particle basis set) if it satisfies the two-particle density equation

$$\langle\Psi|\hat{a}^{pq}_{rs}\hat{H}|\Psi\rangle = \langle\Psi|\hat{a}^{pq}_{rs}|\Psi\rangle\langle\Psi|\hat{H}|\Psi\rangle \quad \forall\ p,q,r,s \tag{5}$$

as this implies that the one-particle density equation is satisfied also. It may be appreciated that the dimension of the Nakatsuji density equation is far lower, in general, than the dimension of the conventional Schrödinger wave equation projected on a finite basis. The number of equations does not depend on the number of electrons but scales instead as the fourth power of the one-particle basis set.

Interestingly, the condition that a normalized wave function is the eigenstate of *some* two-particle Hamiltonian can also be obtained from the Nakatsuji two-particle density equation, and, to my knowledge, this result has not been mentioned before in the literature. Indicating the two-particle operators $\hat{a}^{rs}_{pq}$ generically as $\hat{q}_\lambda$ and writing

$$\hat{H} = \sum_\mu H_\mu \hat{q}_\mu\,, \tag{6}$$

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the density equation can be written as

$$\sum_{\mu} (\langle \Psi | \hat{q}_\lambda \hat{q}_\mu | \Psi \rangle - \langle \Psi | \hat{q}_\lambda | \Psi \rangle \langle \Psi | \hat{q}_\mu | \Psi \rangle) H_\mu = 0 . \tag{7}$$

If we define the quantity in brackets, which amounts to a modified four-particle density matrix, as a matrix $\mathbf{A}$ with elements $A_{\lambda\mu}$ it is seen that the vector of Hamiltonian matrix elements is an eigenvector of $\mathbf{A}$ with eigenvalue 0. The matrix $\mathbf{A}$ can be defined for any wave function, and it follows that a wave function is the eigenfunction of some two-body Hamiltonian if and only if its associated $A$ matrix is singular.

The special nature of eigenfunctions of a two-body Hamiltonian may also be appreciated from another simple argument. In the case of a nondegenerate ground state, the associated two-particle RDM must *uniquely* define (up to a phase factor) the wave function that yields this particular density matrix; otherwise the ground state would be degenerate [7]. It follows from the above argument that a parametrization for the wave function that can access *any* two-particle density matrix is sufficiently flexible to describe the exact (nondegenerate) ground state of the system. In the following, we describe a parametrization of the wave function that is tailored towards the exact description of eigenstates of the Hamiltonian, yet it is not sufficiently flexible to describe an arbitrary state.

From some very general considerations relating to the separability properties and size dependence of the wave function an exponential parametrization appears essential. The exponential ansatz is used in coupled cluster theory [8,9], which has found widespread use as a routinely applicable and highly accurate tool in quantum chemistry (e.g., [10,11]) and physics (e.g., [12]). Let us consider therefore the normalized wave function $|\Psi\rangle = e^{\hat{T}} |\Phi_0\rangle \alpha$. The normalized reference state $|\Phi_0\rangle$ is arbitrary in principle, but in practice it should reasonably approximate the exact eigenstate $|\Psi\rangle$. At this point we will not yet specify the parametrization of $\hat{T}$ but simply consider it to be a general many-body operator. Assuming a complete set of orthonormal states $|\Phi_\lambda\rangle$, which includes $|\Phi_0\rangle$, the Schrödinger equation can be rewritten

$$\begin{aligned} &\langle \Phi_0 | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = E , \\ &\langle \Phi_\lambda | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = 0, \quad \forall\ \lambda \neq 0 , \end{aligned} \tag{8}$$

which resembles the usual single reference coupled cluster (CC) equations, but we note that the operator $\hat{T}$ and the reference state $|\Phi_0\rangle$ are more general here. The CC expression for the energy can be used in the Nakatsuji density equation (5), which then yields

$$\alpha^2 \langle \Phi_0 | e^{\hat{T}^\dagger} \hat{a}^{pq}_{rs} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = \alpha^2 \langle \Phi_0 | e^{\hat{T}^\dagger} \hat{a}^{pq}_{rs} e^{\hat{T}} | \Phi_0 \rangle \times \langle \Phi_0 | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle . \tag{9}$$

The cumbersome normalization factor $\alpha$ is found to cancel, and inserting the resolution of the identity

$$\sum_{\lambda} e^{\hat{T}} | \Phi_\lambda \rangle \langle \Phi_\lambda | e^{-\hat{T}} = \mathbf{1} \tag{10}$$

on the left hand side yields

$$\sum_{\lambda \neq 0} \langle \Phi_0 | e^{\hat{T}^\dagger} \hat{a}^{pq}_{rs} e^{\hat{T}} | \Phi_\lambda \rangle \langle \Phi_\lambda | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = 0 . \tag{11}$$

It is clear that if Eq. (8) holds also the exponential Nakatsuji density equation, Eq. (11), is satisfied. However, the above equation states that it is actually sufficient if a carefully weighted *subset* of the projected CC Schrödinger equation [Eq. (8)] is satisfied.

The Nakatsuji density equation suggests the following parametrization for $\hat{T}$:

$$\hat{T} = t^{rs}_{pq} \hat{a}^{pq}_{rs} . \tag{12}$$

The essential aspect of this parametrization is that the number of parameters equals the number of components in the Nakatsuji density equation. In many branches of physics and quantum chemistry, we simply assume that nonlinear equations like Eq. (11) can be solved, to any degree of accuracy, if the number of parameters equals the number of equations. This would be a far reaching assumption in this instance, however, as it would imply that the eigenstates of a many-body Hamiltonian, containing up to two-body interactions, can be represented exactly by a two-body cluster expansion. However, current mathematics do not provide an answer to the solubility of the above nonlinear equations and at present it seems better to remain silent whereof one cannot speak.

It may be pertinent to clearly distinguish the traditional CC parametrization from the present approach. In exact CC theory the cluster operator needs to include up to $N$-fold excitation operators $\hat{a}^{abc\ldots}_{ijk\ldots}$, for systems containing $N$ electrons, where $i, j, k, \ldots$ label occupied orbitals in the reference *determinant* $|\Phi_0\rangle$, while $a, b, c, \ldots$ label unoccupied orbitals. The various components of the cluster operator commute, and the exponential series terminates explicitly.

The current parametrization (12) is quite different, as $\hat{T}$ is a general two-body *substitution* operator: any pair of orbitals can be replaced by another pair, independent of the occupation of the orbitals in the reference *state* $|\Phi_0\rangle$. The various components in $\hat{T}$ in general do not commute and by connecting various two-body substitution operators one can obtain high rank connected excitation operators. The conjecture is that the higher rank CC excitation operators can be expressed exactly in terms of the general two-body substitution operators. The exponential series does not terminate, and in practice one will have to impose a finite expansion and monitor convergence. The potential exactness of the two-body cluster expansion then means that

one can define a sequence of equations containing additional cluster operators successively, and the sequence of corresponding solutions (if they exist and if the sequence converges) approaches the exact solution in the limit. Finally, the current parametrization may be redundant meaning that different values of $t_\lambda$ yield precisely the same wave function.

In many applications the Hamiltonian has additional symmetry properties, in particular, it may commute with the spin operators $\hat{S}_z, \hat{S}_+, \hat{S}_-$. The number of independent parameters that characterize the Hamiltonian is reduced, therefore implying a reduction of the independent components in the density equation. As a result we can achieve a corresponding reduction in the number of parameters $t_\lambda$ describing the wave function. If we assume the Hamiltonian is real symmetric and the wave function real, a further simplification is possible. The Hamiltonian can be written

$$\hat{H} = \sum_{\lambda \in O} H_\lambda (\hat{q}_\lambda + \hat{q}_\lambda^\dagger) + \sum_{\lambda \in D} H_\lambda \hat{q}_\lambda , \qquad (13)$$

where the operator manifold is split into an off-diagonal, non-Hermitian set $O$, and a diagonal, Hermitian set $D$. Using precisely the same arguments as before, the real wave function is an eigenstate of a real Hermitian Hamiltonian if it satisfies

$$\langle \Psi | (\hat{q}_\lambda^\dagger + \hat{q}_\lambda) \hat{H} | \Psi \rangle = \langle \Psi | (\hat{q}_\lambda^\dagger + \hat{q}_\lambda) | \Psi \rangle E \quad \forall \ \lambda \in O + D . \qquad (14)$$

If this symmetrized density equation is satisfied, the other components of the Nakatsuji density equation are satisfied automatically, and from the reality of the wave function it then follows

$$\langle \Psi | [\hat{H}, (\hat{q}_\lambda - \hat{q}_\lambda^\dagger)] | \Psi \rangle = 0 \quad \forall \ \lambda \in O . \qquad (15)$$

These latter equations are nontrivial, but they are obviously satisfied if $|\Psi\rangle$ is an eigenfunction of the Hamiltonian. Instead of the symmetric density equations (14) it is possible to use Eqs. (15) in addition to the diagonal component $D$ of Eq. (14) to determine the unknown parameters in the wave function.

From the viewpoint of the Nakatsuji density equation a parametrization for $|\Psi\rangle$ can be used that uses precisely the same number of unknowns as there are parameters in the Hamiltonian. This may be of great relevance in the study of a few parameter model Hamiltonians that describe collective phenomena in the solid state, like magnetism and superconductivity. The exact highly nonlinear equations will be very hard to solve and some further approximations are called for.

In connection with Eq. (15) it is appealing to use a unitary exponential transformation that satisfies both an approximate variational principle and preserves size extensivity. The exact solution would require a pseudounitary parametrization

$$|\Psi\rangle = e^{\hat{x}} e^{\tau} |\Phi_0\rangle , \qquad (16)$$

$$\hat{\tau} = \sum_{\lambda \in O} \tau_\lambda (\hat{q}_\lambda - \hat{q}_\lambda^\dagger); \qquad \hat{x} = \sum_{\lambda \in D} \hat{x}_\lambda \hat{q}_\lambda . \qquad (17)$$

The operator $\tau$ is anti-Hermitian, $\hat{\tau}^\dagger = -\hat{\tau}$, such that $e^\tau$ is unitary. Inclusion of the operator $e^{\hat{x}}$ is necessary to supply the required number of parameters, but it is discarded in the analysis below in order to obtain a commutator expansion. This is presumably a sound approximation because according to single reference diagrammatic perturbation theory the diagonal two-body operator $\hat{x}$ would enter first in the third order wave function, and in the fifth order energy. If Eq. (15) is used to provide equations for the parameters $\tau_\lambda$, we obtain

$$\langle \Phi_0 | e^{-\hat{\tau}} [\hat{H}, (\hat{q}_\lambda - \hat{q}_\lambda^\dagger)] e^{\hat{\tau}} | \Phi_0 \rangle = 0 \quad \forall \ \lambda \in O . \qquad (18)$$

Expanding the exponentials one obtains a series of nested commutators, ensuring the size extensivity of the approach even if the commutator series is truncated. If one employs the unitary formulation it is equally possible to use the variational principle to obtain a suitable set of equations

$$E = \langle \Phi_0 | e^{-\hat{\tau}} \hat{H} e^{\hat{\tau}} | \Phi_0 \rangle , \qquad (19)$$

$$\frac{\partial E}{\partial \tau_\lambda} = \frac{\partial}{\partial \tau_\lambda} \langle \Phi_0 | e^{-\hat{\tau}} \hat{H} e^{\hat{\tau}} | \Phi_0 \rangle = 0 \qquad \forall \ \lambda \in O . \qquad (20)$$

Equations (18) and (20) are slightly different and this illustrates an interesting aspect of the Nakatsuji density equation: The CC equations can be weighted arbitrarily, in the sense that

$$\sum_{\lambda \neq 0} z_{rs}^{pq}(\lambda) \langle \Phi_\lambda | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = 0 \qquad (21)$$

will be satisfied if $e^{\hat{T}} |\Phi_0\rangle$ is an exact eigenstate. Independent of the precise choice of weighting factors the solutions $\hat{T}$ that satisfy Eq. (21) include the exact solutions. There may be additional solutions, however, that do not correspond to solutions of the original Nakatsuji density equation and hence do not satisfy the Schrödinger equation. In practice this is not so likely to happen, and we may expect to have substantial freedom to define the precise equations, as long as they are necessarily satisfied by the exact eigenstate, and they can be used to determine (isolated) solutions for the parameters.

In practice, the functional for the energy [Eq. (19)] needs to be truncated and will include a finite set of nested commutators. The variational principle can be applied to this approximate energy functional to obtain a set of working equations. Moreover, one does not need to include *all* operators to achieve high accuracy, and the components in $\hat{\tau}$ can be restricted to those operators that give a nonvanishing result when acting on the "dominant" part of the wave function. The concept of an active orbital space can be used to select a suitable set of operators. It is essential that the various components of $\tau$ do not commute as this feat is responsible for the implicit inclusion of higher excitation effects compared to traditional CC

methods. In addition the reference state $|\Phi_0\rangle$ can be multiconfigurational, facilitating convergence of the commutator series expansion. Recently we have implemented a nonunitary single reference method using a set of two-body substitution operators that is only marginally larger than the set of CC double excitation operators. The resulting Brueckner based generalized coupled cluster method was shown to essentially reproduce full CCSDT results (coupled cluster including single, double, and triple excitations) for small, difficult model systems [13], demonstrating the efficacy of the approach.

In summary, the general two-body exponential representation provides a very compact description of the wave function and the Nakatsuji density equation can be invoked to obtain a well defined set of equations. Such compact parametrizations may be particularly useful to describe highly correlated systems like magnetic transition metal compounds. The application to a few parameter models of collective phenomena in the solid state appears promising, and the potential exactness of the parametrization provides a solid basis for such generalized coupled cluster approaches.

[1] H. Nakatsuji, Phys. Rev. A **14**, 41 (1976).
[2] A. J. Coleman, Rev. Mod. Phys. **35**, 668 (1963).
[3] C. Valdemoro, L. M. Tel, and E. P. Romero, Adv. Quantum Chem. **28**, 33 (1997).
[4] C. Valdemoro, M. P. de Lara-Castells, E. P. Romero, and L. M. Tel, Adv. Quantum Chem. **31**, 37 (1999).
[5] K. Yasuda and H. Nakatsuji, Phys. Rev. A **56**, 2648 (1997).
[6] D. A. Mazziotti, Phys. Rev. A **57**, 4219 (1998).
[7] M. Rosina, in *Reduced Density Operators with Application to Physical and Chemical Systems*, edited by A. J. Coleman and R. M. Erdahl (Queen's University, Kingston, Ontario, Canada, 1968), Vol. 11.
[8] F. Coester, Nucl. Phys. **7**, 421 (1958).
[9] J. Cizek, J. Chem. Phys. **45**, 4256 (1966).
[10] R. J. Bartlett and J. F. Stanton, Rev. Comput. Chem. **5**, 65 (1994).
[11] T. J. Lee and G. E. Scuseria, in *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy,* edited by S. R. Langhoff (Kluwer Academic Publishers, Dordrecht, 1995), p. 47.
[12] R. F. Bishop, Theor. Chim. Acta **80**, 95 (1991).
[13] M. Nooijen and V. Lotrich (to be published).