

Ensuring N -representability: Coleman's algorithm

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Abstract

The energy of a system which is described by a Hamiltonian which includes at most two-particle interactions can be expressed in terms of the second order reduced density matrix. However, for the 2-matrix to have proper symmetry is a weaker condition than requiring that the wavefunction be antisymmetric, which is called the N -representability problem, a problem of long term interest. Coleman [Reduced Density Matrices: Coulson's Challenge, Springer, New York, 2000] however, proposed an algorithm which ensures N -representability. In this Letter we examine the algorithm and show its connection to the full configuration interaction method and the contracted Schroedinger equation. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

For a quantum system with a Hamiltonian involving not more than two-particle interactions it was known as early as in the 1940s that the exact energy of an N -particle system can be expressed in terms of the second order reduced density matrix. That fact aroused the hope of replacing the wavefunction which depends on N particles by the 2-matrix which depends on only two particles and is significantly simpler, particularly in cases of large N . In 1951 Coleman [1] attempted to vary the 2-matrix with respect to the energy and was surprised to find an energy for the lithium atom which was about 20% below the experimental value. The reason for the failure of the variational principle is that

the space of 2-matrices in which he varied was too large. The condition which has to be fulfilled by the 2-matrices is that they correspond to a wavefunction, and that they can be built by integration of that wavefunction N -particle density over $N - 2$ particles. Ensuring this condition is known as the N -representability problem and is currently thought to be an unsolved problem for 2-matrices, though the conditions are well known for 1-matrices.

Balint et al. [2–5] created a two-particle density matrix which is N -representable by construction and used this 2-matrix to obtain fully correlated energies. The exact wavefunction is approximated as a linear combination of Slater determinants $\Psi = \sum_{\alpha=1}^{\mu} c_{\alpha} \Phi_{\alpha}$. The Slater determinants can be expanded in terms of antisymmetrized two-electron functions, geminals g_{ij} , and their co-geminals which leads to a 2-matrix of the form

$$D^2 = \sum_{i < j} \sum_{k < l} g_{ij}(1, 2) g_{kl}^*(1', 2') \Theta_{ij,kl}. \quad (1)$$

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The structure of the matrix Θ corresponds to the anti-symmetric nature of the wavefunction and depends on all expansion coefficients of the wavefunction. Balint et al. developed an efficient algorithm to calculate the factors $\Theta_{ij,kl}$. However, determination of the optimum D^2 requires an optimization with respect to $\binom{M}{N}$ parameters. Balint et al. could reduce the number of parameters to $\binom{M}{2} ((\binom{M}{2}) + 1)/2$ by considering symmetry properties of the system without the introduction of an approximation, but the optimization problem remains formidable.

Coleman [1] used convexity theory to develop an algorithm which ensures N -representability. He showed that the energy can be expressed in terms of the elements of the polar space of all 2-matrices. By applying conditions to those elements, the space of N -representable 2-matrices can be found. The proposed formalism involves the solution of large determinantal equations, however.

In the following section, Coleman's algorithm is presented followed by a discussion of its realization and its connection to the full configuration interaction problem and the contracted Schrödinger equation. In the appendix, we illustrate Coleman's algorithm on the example of Helium.

2. Coleman's algorithm

Coleman's challenge was to formulate the 2-matrix without reference to a wavefunction, but yet still be derivable from one, and to use that 2-matrix to calculate the energy. By applying convexity theory, Coleman was able to express the exact 2-matrices in terms of the elements of their polar cone for which he was able to describe its boundary. The following is a sketch of Coleman's derivation, details can be found in [1].

The Hamiltonian is

$$H = \sum_i^N v(i) + \sum_{(i>j)}^N w(i, j) \quad (2)$$

with v being the one-particle kinetic energy and electron nuclear attraction operator and w being the two-particle electron–electron repulsion operator which depends on N particles. It can be re-

duced to contain only two particles by making use of the identity of the particles and the fact that the Hamiltonian does not include more than two-particle interactions

$$K = v(1) + v(2) + (N - 1)w(1, 2). \quad (3)$$

The exact energy is then given in terms of K and the second order reduced density matrix

$$E = \frac{1}{2}N \operatorname{tr}(KD^2). \quad (4)$$

The n th order density matrices D^n are normalized to 1 and defined by

$$D^n = \int \Psi^*(1', \dots, n', n + 1, \dots, N) \times \Psi(1, \dots, n, n + 1, \dots, N) dx_{n+1} \cdots dx_N. \quad (5)$$

We assume that all spaces can be spanned by products of a complete orthonormal basis of the one-dimensional Hilbert space of one-particle functions. According to von Neumann, the state of a quantum system is characterized by a positive operator, D^N , of unit trace acting on Fock space. The sum of two bounded positive operators is a positive operator, which is the definition for a convex set. Therefore, the set of all von Neumann density operators for a system of N particles is convex. The scalar product of two linear operators A and B acting on the N -dimensional Hilbert space is taken to be the trace scalar product $(A|B)_N := \operatorname{tr}(A^+B)$.

The polar cone of the p th order reduced density matrices, the Kummer cone \mathcal{K}_N^p , is defined from the elements of the Kummer cone B^p . The Kummer cone is defined by

$$\mathcal{K}_N^p := \{B^p | \forall \widetilde{D}^p \operatorname{tr}(B^p \widetilde{D}^p) \geq 0\}. \quad (6)$$

\widetilde{D}^p indicates that the normalization condition does not need to be satisfied. The Bipolar Theorem states that the polar cone of the polar cone is the cone itself. Therefore, we conclude that an operator of trace 1 is a p th order density operator if and only if

$$\operatorname{tr}(B^p \widetilde{D}^p) \geq 0 \quad \text{for all } B^p \in \mathcal{K}_N^p. \quad (7)$$

But it can be shown that Eq. (7) is equivalent to the requirement that B^p be a positive operator.

Coleman used Kummer's expansion operator Γ_p^N which transforms an operator which acts on a

p -dimensional space into an operator acting on the N -dimensional space, i.e. $B^N = \Gamma_p^N(B^p)$. Furthermore, it can be shown that the gradient of $|B^N| = |\Gamma_p^N(B^p)|$ under the normalization condition

$$\text{tr}\left(\frac{\partial|B^N|}{\partial B^p}\right) = 1 \quad (8)$$

is a p th order reduced density operator. That enables us to rewrite Eq. (4) in terms of the elements of the Kummer cone if condition (8) is fulfilled

$$E = \frac{1}{2}N \text{tr}\left(\frac{\partial|B^N|}{\partial B^2}K\right). \quad (9)$$

Since positive multiples of the identity operator are interior to the Kummer cone, a possible strategy for finding the ground state energy is to initialize B^2 as a multiple of I^2 and move towards the boundary in a direction which decreases the value of E while maintaining the normalization condition.

Coleman [1] proposed to use an ansatz for B^2 which was suggested by Erdahl and Davidson

$$B^2 = \alpha I^2 + \beta \frac{N}{2} K^2. \quad (10)$$

Applying the expansion operator, Γ_2^N , we are led to

$$\begin{aligned} \Gamma_2^N(B^2) &= B^N = \alpha \Gamma_2^N(I^2) + \beta \frac{N}{2} \Gamma_2^N(K^2) \\ &= \alpha I^N + \beta H. \end{aligned} \quad (11)$$

Let us choose α and β such that $|B^N| = 0$ and $\text{tr}(\partial|B^N|/\partial B^2) = 1$, which restricts the solutions to be points on the surface of the Kummer cone which correspond to normalized N -representable 2-matrices. For a nondegenerate state, $|B^N| = 0$ implies that the adjugate of B^N has rank 1 and is proportional to the projector onto Ψ . Therefore, $B^N \Psi = 0$. Multiplying Eq. (11) by Ψ gives:

$$B^N \Psi = \alpha I^N \Psi + \beta H \Psi = 0, \quad (12)$$

$$H \Psi = -\frac{\alpha}{\beta} \Psi. \quad (13)$$

It is apparent that $-\alpha/\beta$ is an eigenvalue of H . We choose further $\alpha = 1$.

Conversely, if

$$H \Psi = \lambda \Psi, \quad (14)$$

then $B^N \Psi = 0$ and $|B^N| = 0$. Thus the eigenvalues of H are precisely the zeros of $|B^N|$ and $\lambda = -\alpha/\beta$. However, it is not, in principle, necessary to diagonalize the matrix or variationally optimize the solutions, i.e. introduce a wavefunction.

In order to calculate $|B^N|$ Coleman suggested the following procedure. Express K^2 and I^2 in a basis of anti-symmetrized two-electron functions (geminals) built from an orthonormal one-electron function basis of order M . Adding the two matrices gives B^2 expressed in a Slater geminal basis. Find B^N in terms of B^2 by application of the expansion operator, B^N is a $s_N \times s_N$ symmetric matrix, with $s_N = \binom{M}{N}$. Solve for the roots of the polynomial obtained by setting the determinant of B^N equal to zero. Denote the elements of the matrix B^2 by B_v^μ , where μ and ν represent pairs of integer labeling the $s_2 = \binom{M}{2}$ Slater geminals of the basis for the two-particle space. Then the two matrix of the state is obtained by differentiating the determinant $|B^N|$ with respect to the B_v^μ 's. The difference between the rank of B^N (s_N) and B^2 (s_2) is a measure of the potential advantage of his algorithm over a full CI approach.

How to obtain the B^N matrix from the B^2 matrix according to Coleman is illustrated on the simplest example of $M = 4$ and $N = 3$. B^N is then a 4×4 matrix. Order the $s_N = 4$ configurations from 1 to 4, $1 = (123)$, $2 = (124)$, $3 = (134)$, $4 = (234)$. Setting $s = (N/2)\beta$, the matrix elements of B^N are then:

$$\begin{aligned} B_{1,1}^N &= B_{12}^{12} + B_{13}^{13} + B_{23}^{23}, \\ B_{1,2}^N &= B_{14}^{13} + B_{24}^{23}, \\ B_{1,3}^N &= B_{41}^{12} + B_{34}^{23}, \\ &\dots \end{aligned}$$

with

$$\begin{aligned} B_{12}^{12} &= 1 + sK_{12}^{12}, \\ B_{14}^{13} &= sK_{14}^{13}, \\ &\dots \\ K_{12}^{12} &= (1|h|1) + (2|h|2) + (11|22) - (12|12), \\ K_{14}^{13} &= (3|h|4) + (11|34) - (13|14), \\ &\dots \end{aligned}$$

From each diagonal element of B^2 one picks up a summand of 1 in the diagonal elements of B^N . The

number of diagonal elements of B^2 contributing to each diagonal element of B^N is $r = \binom{N}{2}$. The above recipe implies that the operator which is added to βH to obtain B^N is not the identity operator as in Eq. (12) but the identity operator multiplied by r , denoted by I_r^N . To compensate for that, α needs to be set to $1/r$ and not to 1 as originally formulated in Coleman's algorithm.

However finding the roots of a polynomial of the order s_N obtained by setting the determinant of B^N equal to zero is difficult, and though not necessary from a variational or wavefunction viewpoint, the polynomial can be converted into an eigenvalue problem:

$$B_{i,i}^N = r + s \sum_{k,l \in i}^p K_{kl}^{kl}, \quad (15)$$

$$B_{i,j}^N = s \sum_{k < l \in i, m < n \in j} (-1)^\sigma K_{mn}^{kl} \\ \forall i - \{k, l\} = j - \{m, n\}. \quad (16)$$

Here i and j denote configurations which are elements of the N -dimensional Hilbert-space whereas k, l, m, n are one-electron functions in the one-dimensional Hilbert-space. The sum in Eq. (16) runs only over such $k, l \in i$ and $m, n \in j$ for which the remaining 3 to N functions are identical. σ is the number of permutations necessary to reorder the configurations such that the order of $i - \{k, l\}$ and $j - \{m, n\}$ is the same. Notice that since $(N/2)K^2 = H$, the sum of elements of K^2 occurring in the elements of B^N amounts to the same integrals, then each element of H in the basis of configurations does, and we have

$$|B^N| = |I_2^N(I^2 + sK^2)|, \quad (17)$$

$$= \left| \frac{1}{r} I_r^N + \beta H \right|, \quad (18)$$

$$= |I^N + \beta H|, \quad (19)$$

$$= \beta^{s_N} \left| \frac{1}{\beta} I^N + H \right| = 0. \quad (20)$$

For $\beta \neq 0$ Eq. (20) is equivalent to:

$$\left| \frac{1}{\beta} I^N + H \right| = 0. \quad (21)$$

Set $\lambda = -1/\beta$

$$|H - \lambda I^N| = 0. \quad (22)$$

B^N , I and H are expressed in the basis of configurations and Eq. (22) describes the eigenvalue problem of $H\Psi = E\Psi$ if $E = \lambda$ and $\Psi = \sum_{i=1}^{s_N} c_i i$, Ψ is a linear combination of configurations. Therefore finding the roots of the polynomial from setting $|B^N| = 0$ is exactly equivalent to finding the eigenvalues of a configuration interaction problem. Having the eigenvalues found, the eigenvectors are the wavefunction. Although diagonalization can be one step more difficult in principle, in practice there seems to be no advantage of Coleman's algorithm over full CI since the problem to be solved seems to be diagonalization of a $s_N \times s_N$ matrix as well as it is for full CI, even though the variational condition of full CI need not be imposed in the algorithm. Diagonalizing the configuration interaction matrix is formally a problem which scales with s_N^3 , with s_N being the number of configurations. However, one is in general not interested in obtaining all the eigenvalues of the configuration interaction matrix but only a few of them, let us say t . In quantum chemical programs the diagonalization of the CI matrix is most efficiently realized in an iterative manner and scales with $t s_N^2$. Furthermore, by virtue of forming repeated $\mathbf{H}\sigma$ products [8], which correspond to a series of matrix vector products, only a few of the latter are required in the iterative diagonalization methods of Lanczos [6], Nesbet [7], Bartlett [8] and Davidson [9] to construct the t -dimensional mini-matrix of vectors for diagonalization. Furthermore, in this manner there is no need to store \mathbf{H} which has an exorbitant dimension, but instead evaluate the series of vectors on the fly.

However, an interesting question to ask is if the combination of Coleman's algorithm together with the contracted Schroedinger equation could lead to new approximations to the density equation? The density equation relates the n th order reduced density matrix to the $(n+1)$ th and $(n+2)$ th order reduced density matrices, introduced in 1976 by Cohen and Frishberg [10] and Nakatsuji [11]. Nakatsuji proved in his paper that a necessary and sufficient condition for Ψ to satisfy the Schroe-

dinger equation is given by the solution of the density equation

$$\begin{aligned}
 ED^n = & \left(\sum_i^n v(i) + \sum_{i>j}^n w(i, j) \right) D^n + (N - n) \\
 & \times \int \left(v(n + 1) + \sum_i^n w(i, n + 1) \right) \\
 & \times D^{(n+1)} dx_{n+1} + \frac{(N - n)(N - (n + 1))}{2} \\
 & \times \int w(n + 1, n + 2) D^{(n+2)} dx_{n+1} dx_{n+2}. \quad (23)
 \end{aligned}$$

For $n \geq 2$ every density equation is equivalent to the Schroedinger equation if D^n , $D^{(n+1)}$ and $D^{(n+2)}$ are N -representable. However, using the reduced density matrices directly as variables to circumvent the need for a wavefunction is not an easy task, since the number of unknowns in Eq. (23) exceeds the number of conditions, as the n th order density equation contains the n th, $(n + 1)$ th and $(n + 2)$ th order reduced density matrices.

The density equation gives a prescription of how to obtain a reduced density matrix of a given order in terms of higher order reduced density matrices. Different decoupling approximations of the higher order density matrices have been suggested by Valdemoro and co-workers [12–20], Nakatsuji et al. [21–25] and Mazziotti [26–28]. However, the N -representability of the resulting density matrices is not guaranteed, depending on the quality of the scheme for approximating the higher order reduced density matrices, consequently, the solutions are not necessarily physically meaningful.

If we consider the density equation for $n = 2$ for simplicity, in order to apply Coleman's algorithm we need to express the 3-matrix and the 4-matrix in terms of the elements of the Kummer cone. Since the gradient of $|B^N|$ with respect to B^p under the condition $\text{tr}(\partial|B^N|/\partial B^p) = 1$ is the p th order reduced density operator, the third and fourth order reduced density operators are given by:

$$D^3 = \frac{\partial|B^N|}{\partial B^3} \text{ with } \text{tr} \left(\frac{\partial|B^N|}{\partial B^3} \right) = 1, \quad (24)$$

$$D^4 = \frac{\partial|B^N|}{\partial B^4} \text{ with } \text{tr} \left(\frac{\partial|B^N|}{\partial B^4} \right) = 1. \quad (25)$$

for B^N being the corresponding element of D^N in the Kummer cone. Using Eq. (10) B^3 and B^4 are obtained by applying the expansion operator Γ_p^N

$$B^3 = \Gamma_3^N(B^2) = \alpha \Gamma_3^N(I^2) + \beta \frac{N}{2} \Gamma_3^N(K^2), \quad (26)$$

$$B^4 = \Gamma_4^N(B^2) = \alpha \Gamma_4^N(I^2) + \beta \frac{N}{2} \Gamma_4^N(K^2). \quad (27)$$

B^3 is expressed in an anti-symmetrized three-electron function basis derived from the functions spanning the one-dimensional Hilbert-space, B^4 in an anti-symmetrized four-electron function basis. The expansions of B^2 to B^3 and to B^4 follow the same rules as the expansion of B^2 to B^N illustrated on the example above, but it is in general significantly simpler. The reduced density matrices having the same basis as B^3 and B^4 , respectively, can be obtained through Eqs. (24) and (25).

The density equation for $n = 2$ can then be rewritten

$$\begin{aligned}
 E \left(\frac{\partial|B^N|}{\partial B^2} \right) = & (v(1) + v(2) + w(2, 1)) \left(\frac{\partial|B^N|}{\partial B^2} \right) \\
 & + (N - 2) \int (v(3) + w(1, 3) \\
 & + w(2, 3)) \left(\frac{\partial|B^N|}{\partial B^3} \right) dx_3 \\
 & + \frac{(N - 2)(N - 3)}{2} \\
 & \times \int w(3, 4) \left(\frac{\partial|B^N|}{\partial B^4} \right) dx_3 dx_4, \quad (28)
 \end{aligned}$$

where the trace conditions have to be fulfilled. Eq. (28) can be easily generalized to $n > 2$. Eq. (28) and unlike other approximations to the density equation, its generalizations are exact. With a given ansatz for B^2 , like Eq. (10), the only unknown in Eq. (28) is B^N . It might be possible to find reasonable but simpler approximations to B^N which might provide an efficient way to calculate the energy and the 2-matrix of the system.

3. Summary

We have shown that solving for all roots of the polynomial equation obtained from setting the

determinant of B^N equal to zero as suggested by Coleman is equivalent to solving the full Configuration Interaction problem. Solving for all roots of a polynomial of very high degree, namely the dimension of the configurational space of the problem, is an extremely inefficient procedure, raising the issue of any practical advantage over diagonalization, even though the latter adds a redundant variational condition.

Coleman's algorithm does not require solving for all roots of the polynomial. Hence, it is possible that one can exploit that fact and find numerical procedures which are more efficient than diagonalization. However, today, the routine ease in extracting a few eigenvalues and vectors for matrices whose dimension exceeds 10^7 , argues that iterative diagonalization is likely to be preferable anyway.

We have also shown the connection between Coleman's algorithm and the contracted Schrödinger equation. In the appendix we give as an example of how Coleman's algorithm is applied to the case of Helium.

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Appendix A

How Coleman's algorithm is applied is shown on the example of Helium in the following section.

The simplest example to recover correlation energy is to expand the one-dimensional Hilbert space with four spin functions. That allows in the language of configuration interaction for single and double excitations. Following Coleman's algorithm should then be equivalent to a full CI approach in the basis of those four spin functions. The four orthonormal spin functions are chosen to be Hartree-Fock molecular orbitals obtained from a Hartree-Fock calculation with a 3-21G basis set: $\varphi_1 = \phi_1\alpha$, $\varphi_2 = \phi_1\beta$, $\varphi_3 = \phi_2\alpha$ and $\varphi_4 = \phi_2\beta$. With that choice it is possible to form six Slater geminals:

(12), (13), (14), (23), (24), (34). Since (13) has a spin combination ($\alpha\alpha$) and (24) has a spin combination ($\beta\beta$) those two Slaters were excluded. To build B^2 , K^2 and I^2 have to be expressed in terms of the Slater geminals. Since the geminals are normalized, the matrix representation of I^2 is the unit matrix. B^2 is symmetric and has the following form:

$$B^2 = \begin{pmatrix} 1 + sK_{12}^{12} & sK_{14}^{12} & sK_{23}^{12} & sK_{34}^{12} \\ sK_{14}^{12} & 1 + sK_{14}^{14} & sK_{23}^{14} & sK_{34}^{14} \\ sK_{23}^{12} & sK_{23}^{14} & 1 + sK_{23}^{23} & sK_{34}^{23} \\ sK_{34}^{12} & sK_{34}^{14} & sK_{34}^{23} & 1 + sK_{34}^{34} \end{pmatrix} \quad (\text{A.1})$$

with

$$K_{12}^{12} = 2(\phi_1|v|\phi_1) + (\phi_1\phi_1|\phi_1\phi_1),$$

$$K_{14}^{14} = (\phi_1|v|\phi_1) + (\phi_2|v|\phi_2) + (\phi_1\phi_1|\phi_2\phi_2),$$

$$K_{23}^{23} = (\phi_1|v|\phi_1) + (\phi_2|v|\phi_2) + (\phi_1\phi_1|\phi_2\phi_2),$$

$$K_{34}^{34} = 2(\phi_2|v|\phi_2) + (\phi_2\phi_2|\phi_2\phi_2),$$

$$K_{14}^{12} = (\phi_1|v|\phi_2) + (\phi_1\phi_1|\phi_1\phi_2),$$

$$K_{23}^{12} = -(\phi_1|v|\phi_2) - (\phi_1\phi_2|\phi_1\phi_1),$$

$$K_{34}^{12} = (\phi_1\phi_2|\phi_1\phi_2),$$

$$K_{23}^{14} = -(\phi_1\phi_2|\phi_1\phi_2),$$

$$K_{34}^{14} = (\phi_1|v|\phi_2) + (\phi_1\phi_2|\phi_2\phi_2),$$

$$K_{34}^{23} = -(\phi_1|v|\phi_2) - (\phi_1\phi_2|\phi_2\phi_2).$$

The integrals are given in Mulliken notation.

In the special case of Helium B^2 equals B^N . Setting B^2 equal to zero results in a polynomial of degree 4. We solved for the roots of the polynomial. The smallest positive root is 0.35082 and corresponds to the ground state energy which was found to be -2.85058 a.u. which is indeed the full CI energy.

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