Appendix A

N-representability

In the minimization of the total energy with respect to the one-body reduced density matrix one has to ensure that all density matrices can be represented by an ensemble of properly anti-symmetrized N-particle wave functions. This problem is known as the N-representability problem. The constraints for the one-body reduced density matrix

$$\Gamma^{(1)} = \sum_{j=1}^{\infty} n_j \varphi_j^*(\mathbf{r}) \varphi_j(\mathbf{r}) \tag{A.1}$$

to be indeed ensemble N-representable are given by

$$0 \leq n_j \leq 1, \quad \sum_{j=1}^{\infty} n_j = N. \tag{A.2}$$

Although these conditions are relatively simple, the proof that they are in fact necessary *and* sufficient [47] is rather involved. In the following, we review the proof and in particular discuss the distinction between pure-state and ensemble N-representability. Although the proof by Coleman [47] contains both the necessity as well as the sufficiency of the two conditions, the necessity can also be proven in a more intuitive way given by Löwdin [83].

Following Löwdin we expand the many-body wave function Ψ in Slater determinants using the natural orbitals, i.e.

$$\Psi(\mathbf{x}_1...\mathbf{x}_N) = \sum_K c_K \, \Phi_K(\mathbf{x}_1...\mathbf{x}_N), \tag{A.3}$$

$$\Phi_K(\mathbf{x}_1...\mathbf{x}_N) = \frac{1}{\sqrt{N!}} \det\{\varphi_{k_1}, \varphi_{k_2}, ...\varphi_{k_N}\}, \tag{A.4}$$

where $K = \{k_i \text{ with } k_i < k_{i+1}\}$ denotes the ordered set of orbitals appearing in determinant K. The normalization of the many-body wave function results in

$$\sum_K \mid c_K \mid^2 = 1. \tag{A.5}$$

The 1-RDM for the wave function (A.3) is then given by

$$
\begin{aligned}
\Gamma^{(1)}(\mathbf{x}_1; \mathbf{x}_1') &= N \sum_{K,L} c_K^* c_L \int d\mathbf{x}_2...d\mathbf{x}_N \, \Phi_K^*(\mathbf{x}_1'...\mathbf{x}_N)\Phi_L(\mathbf{x}_1...\mathbf{x}_N) \\
&= \sum_{K,L} c_K^* c_L \sum_{k \in K} \sum_{l \in L} \varphi_k^*(\mathbf{x}_1')\varphi_l(\mathbf{x}_1) D_{KL}(k,l).
\end{aligned} \tag{A.6}
$$

Here, $D_{KL}(k,l)$ is the minor of first order of

$$
D_{KL} = \int d\mathbf{x}_1...d\mathbf{x}_N \, \Phi_K^*(\mathbf{x}_1...\mathbf{x}_N)\Phi_L(\mathbf{x}_1...\mathbf{x}_N). \tag{A.7}
$$

Changing the order of summation in (A.6) we obtain

$$
\Gamma^{(1)}(\mathbf{x}_1; \mathbf{x}_1') = \sum_{k,l} \varphi_k^*(\mathbf{x}_1')\varphi_l(\mathbf{x}_1) \sum_{K \ni k} \sum_{L \ni l} c_K^* c_L D_{KL}(k,l), \tag{A.8}
$$

where the second summation runs over all determinants K (L) that contain the orbital k (l). Hence, one finds the standard expression for the 1-RDM

$$
\Gamma^{(1)}(\mathbf{x}_1; \mathbf{x}_1') = \sum_k n_k \varphi_k^*(\mathbf{x}_1')\varphi_k(\mathbf{x}_1) \tag{A.9}
$$

with the occupation number

$$
n_k = \sum_{K \ni k} \sum_{L \ni k} c_K^* c_L D_{KL}(k,k). \tag{A.10}
$$

For $k \neq l$, there is no contribution to the sum because we have chosen to work with natural orbitals. The first order minor $D_{KL}(k,k)$ reduces to a Kronecker-Delta δ_{KL} and, hence,

$$
n_k = \sum_K^{(k)} \mid c_K \mid^2. \tag{A.11}
$$

Since the sum runs only over those coefficients c_K where the respective determinant contains the orbital k we find $0 \leq n_k \leq 1$ from the normalization (A.5). The summation over k

$$
\sum_{k=1}^{\infty} n_k = \sum_{k=1}^{\infty} \sum_K^{(k)} \mid c_K \mid^2 = \sum_K \sum_k^K \mid c_K \mid^2 = \sum_K N \mid c_K \mid^2 = N \tag{A.12}
$$

shows that the second condition is fulfilled as well. Therefore, we conclude that any normalized anti-symmetric wave function Ψ leads to a $\Gamma^{(1)}$ in agreement with (A.2) (hence the conditions are necessary to ensure N-representability).

In a second step we now show that the conditions are sufficient. This proof relies on properties of compact convex sets. A set $\mathcal{S}$ is called convex iff for any two elements $A, B \in \mathcal{S}$ one finds

$$\alpha A + (1 - \alpha)B \in \mathcal{S}, \quad \forall\, 0 \leq \alpha \leq 1. \tag{A.13}$$

According to the Krein-Milman theorem [48] a convex set is completely determined by its extreme elements. An element A is extreme iff from

$$A = \alpha B + (1 - \alpha)C, \quad 0 < \alpha < 1 \tag{A.14}$$

follows $B = a_1 A$, $C = a_2 A$, i.e. both B and C are multiples of A. If the elements of the set are normalized ($\| A \| = 1$), one can conclude that $B = C = A$. In order to employ the Krein-Milman theorem we first show that the set of ensemble N-representable density matrices $\mathcal{P}_N^{(1)}$ is convex. An ensemble N-representable 1-RDM is given as a sum over pure-state RDMs

$$\Gamma^{(1)}(\mathbf{x}_1; \mathbf{x}_1') = \sum_j c_j \Gamma_j^{(1)}(\mathbf{x}_1; \mathbf{x}_1'), \tag{A.15}$$

where each $\Gamma_j^{(1)}(\mathbf{x}_1; \mathbf{x}_1')$ is connected to a pure-state wave function Ψ_j via

$$\Gamma^{(1)}(\mathbf{x}_1; \mathbf{x}_1') = N \int d\mathbf{x}_2...d\mathbf{x}_N \Psi_j^*(\mathbf{x}_1', \mathbf{x}_2...\mathbf{x}_N)\Psi_j(\mathbf{x}_1, \mathbf{x}_2...\mathbf{x}_N). \tag{A.16}$$

The coefficients satisfy

$$0 \leq |c_j| \leq 1, \quad \sum_j |c_j|^2 = 1. \tag{A.17}$$

In order to show that $\mathcal{P}_N^{(1)}$ is convex we form a weighted average in the sense of (A.13) of two matrices (A.15). This weighted average is simply the 1-RDM of another ensemble and hence again an element of the set $\mathcal{P}_N^{(1)}$. In contrast to ensemble N-representable matrices, the set of pure state N-representable matrices is not necessarily convex. Therefore, we have to work with ensembles. Löwdin's proof for the conditions (A.2) to be necessary can be extended to ensembles by adding the appropriate sums over pure-states.

In the next step we discuss the extreme elements of the set $\mathcal{P}_N^{(1)}$. We claim that the extreme elements of $\mathcal{P}_N^{(1)}$ are 1-RDMs corresponding to single Slater determinants

$$\Psi_S(\mathbf{x}_1...\mathbf{x}_N) = \frac{1}{\sqrt{N!}} \det\{\varphi_{k_1}...\varphi_{k_N}\}, \tag{A.18}$$

i.e.

$$\Gamma_S^{(1)}(\mathbf{x}_1; \mathbf{x}_1') = \sum_{j=1}^{N} \varphi_{k_j}^*(\mathbf{x}_1')\varphi_{k_j}(\mathbf{x}_1). \tag{A.19}$$

We write $\Gamma_S^{(1)}$ as a weighted average of two 1-RDM $\Gamma_1^{(1)}$ and $\Gamma_2^{(1)}$ which are both elements of $\mathcal{P}_N^{(1)}$, i.e.

$$\Gamma_S^{(1)}(\mathbf{x}_1; \mathbf{x}_1') = \alpha \Gamma_1^{(1)}(\mathbf{x}_1; \mathbf{x}_1') + (1 - \alpha) \Gamma_2^{(1)}(\mathbf{x}_1; \mathbf{x}_1'). \qquad (A.20)$$

The rank of $\Gamma_S^{(1)}$, i.e. the number of its non-zero eigenvalues, is equal to the particle number N. For $\Gamma_1^{(1)}$ and $\Gamma_2^{(1)}$ to be in $\mathcal{P}_N^{(1)}$ it is necessary that their eigenvalues fulfil $0 \leq n_j \leq 1$. Therefore, the rank of $\Gamma_1^{(1)}$ and $\Gamma_2^{(1)}$ is at least N due to $\sum_j n_j = N$. Actually, it is equal to N if and only if N occupation numbers of $\Gamma_1^{(1)}$ and $\Gamma_2^{(1)}$ are equal to 1 and the rest are zero which again resembles single Slater determinants. The rank of a matrix is identical to the dimension of the range of this matrix. The dimension of the range of the sum of two matrices is identical to the dimension of the union of the two ranges of the single matrices. Therefore, we can conclude that the rank of $\Gamma_S^{(1)}$ is bigger or equal to N. The equivalence only holds true if the ranges of $\Gamma_1^{(1)}$ and $\Gamma_2^{(1)}$ are identical and of dimension N. In other words, both $\Gamma_1^{(1)}$ and $\Gamma_2^{(1)}$ represent a single Slater determinant with the same set of orbitals, i.e. $\Gamma_1^{(1)} = \Gamma_2^{(1)} = \Gamma_S^{(1)}$. Hence, $\Gamma_S^{(1)}$ is an extreme element of $\mathcal{P}_N^{(1)}$. The question remains if there are other extreme elements.

We assume that there exists a $\Gamma^{(1)}$ which is an extreme element but does not correspond to a single Slater determinant. Expanding the wave function corresponding to this $\Gamma^{(1)}$ in Slater determinants we find

$$\Gamma^{(1)}(\mathbf{x}_1; \mathbf{x}_1') = \sum_k c_k \Gamma_{Sk}^{(1)}(\mathbf{x}_1; \mathbf{x}_1'), \qquad (A.21)$$

where $\Gamma_{Sk}^{(1)}$ again denote 1-RDMs from single Slater determinants. Due to normalization the coefficients c_k have to sum up to 1 and, hence, Eq. (A.21) is a weighted average. If $\Gamma^{(1)}$ is an extreme element, $\Gamma^{(1)} = \Gamma_{Sk}^{(1)}$ for all k which contradicts the assumption that $\Gamma^{(1)}$ is not representing a single Slater determinant.

We have shown that the extreme elements of $\mathcal{P}_N^{(1)}$ are one-body density matrices corresponding to single Slater determinants. We now leave $\mathcal{P}_N^{(1)}$ for a moment and consider the space of functions μ

$$\mathcal{J}_N = \left\{ \mu(\mathbf{x}; \mathbf{x}') \mid \mu(\mathbf{x}; \mathbf{x}') = \sum_{j=1}^{\infty} n_j \phi_j^*(\mathbf{x}') \phi_j(\mathbf{x}), 0 \leq n_j \leq 1, \sum_{j=1}^{\infty} n_j = N \right\}, \quad (A.22)$$

i.e. $\mathcal{J}_N$ represents all density matrices with occupation numbers between zero and one summing up to the particle number N. The orbitals ϕ_j represent a complete set of orthonormal orbitals. This set can differ for different elements of the set, i.e. the elements are diagonal in different basis sets. In the remainder of this section we show that the set $\mathcal{J}_N$ is convex and has the same extreme elements as $\mathcal{P}_N^{(1)}$. The two sets are therefore identical.

First, we have to show that the set $\mathcal{J}_N$ is convex. If we form a weighted average of two elements of $\mathcal{J}_N$

$$\mu(\mathbf{x}; \mathbf{x}') = \alpha\nu(\mathbf{x}; \mathbf{x}') + (1 - \alpha)\tau(\mathbf{x}; \mathbf{x}') \tag{A.23}$$

we can expand the orbitals of ν and τ in those of μ

$$\phi_j^\nu = \sum_{k=1}^\infty c_{jk}^\nu \phi_k^\mu \tag{A.24}$$

$$\phi_j^\tau = \sum_{k=1}^\infty c_{jk}^\tau \phi_k^\mu \tag{A.25}$$

which results in

$$\mu(\mathbf{x}; \mathbf{x}') = \sum_{j,k,l=1}^\infty \left(\alpha\, n_j^\nu\, c_{jk}^{*\nu} c_{jl}^\nu + (1 - \alpha)\, n_j^\tau\, c_{jk}^{*\tau} c_{jl}^\tau\right) \phi_k^{*\mu}(\mathbf{x}')\phi_l^\mu(\mathbf{x}) \tag{A.26}$$

$$= \sum_{k=1}^\infty n_k^\mu \phi_k^{*\mu}(\mathbf{x}')\phi_k^\mu(\mathbf{x}). \tag{A.27}$$

The occupation numbers of μ are hence given as

$$n_k^\mu = \alpha \sum_{j=1}^\infty n_j^\nu \mid c_{jk}^\nu \mid^2 +(1 - \alpha)\sum_{j=1}^\infty n_j^\tau \mid c_{jk}^\tau \mid^2, \tag{A.28}$$

and the off-diagonal terms in the first sum have to vanish because we chose to expand in the natural orbitals of μ. From the normalization of all three basis sets, the restrictions for the occupation numbers of ν and τ, and $0 < \alpha < 1$, one can see that the resulting occupation numbers n_k^μ are indeed again between zero and one. Therefore, μ is an element of $\mathcal{J}_N$ which, as a consequence, is convex.

As the final part of the proof we show that the extreme elements of $\mathcal{J}_N$ are those functions μ with N of the n_j equal to 1 and the remaining n_j equal to zero. We, again, first show that these elements are indeed extreme before we prove that no other extreme elements exist. We write the extreme element μ again as a weighted average

$$\mu(\mathbf{x}; \mathbf{x}') = \alpha\nu(\mathbf{x}; \mathbf{x}') + (1 - \alpha)\tau(\mathbf{x}; \mathbf{x}') \tag{A.29}$$

with $\nu, \tau \in \mathcal{J}_N$. Being elements of $\mathcal{J}_N$ both the ranges of ν and τ have dimensions equal or larger than N. Since the dimension of the range of μ is identical to N, by assumption, we can conclude, using the same arguments as for the set $\mathcal{P}_N^{(1)}$, that both ν and τ can be simultaneously diagonalized and have N occupation numbers which are equal to one. Hence, $\nu = \tau = \mu$ and, therefore, μ is an extreme element.

Now we assume that there exists an extreme element μ which is not of the above type. Without loss of generality we assume that the n_j^μ are ordered such that

$$1 \geq n_1^\mu \geq n_2^\mu... \geq n_{N+1}^\mu... \geq 0. \tag{A.30}$$

Then there exists an $\epsilon > 0$ such that

$$0 < \epsilon < n_N^\mu, \tag{A.31}$$

$$n_{N+1}^\mu < 1 - \epsilon. \tag{A.32}$$

We can then decompose μ into

$$\mu(\mathbf{x}; \mathbf{x}') = \epsilon \nu(\mathbf{x}; \mathbf{x}') + (1 - \epsilon)\tau(\mathbf{x}; \mathbf{x}'), \tag{A.33}$$

where $n_j^\nu = 1$ for $j \leq N$ and $n_j^\nu = 0$ otherwise, and the occupation numbers of τ are then given by

$$n_j^\tau = \frac{n_j^\nu - \epsilon}{1 - \epsilon}, \quad j \leq N, \tag{A.34}$$

$$n_j^\tau = \frac{n_j^\nu}{1 - \epsilon}, \quad j > N. \tag{A.35}$$

In both cases one can show that $0 \leq n_j^\tau \leq 1$, and also

$$\sum_{j=1}^\infty n_j^\tau = N. \tag{A.36}$$

Therefore, we can conclude that $\tau \in \mathcal{J}_N$. The element μ can therefore be written as the weighted average of two elements of $\mathcal{J}_N$ which are different from μ. Hence, μ is not extreme.

Furthermore, we know that the extreme elements μ correspond to single Slater determinants via Eq. (2.9). We have hence proven that the extreme elements of $\mathcal{J}_N$ and $\mathcal{P}_N^{(1)}$ are identical. Due to the convexity of both sets and the Krein-Milman theorem [48], the two sets are identical, which proves that the conditions (A.2) are indeed necessary and sufficient for a 1-RDM to be ensemble N-representable.