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The N-Representability Problem and Orbital Occupation in Transition Metals

by

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Declaration of Authorship

I hereby declare that the work presented here is original and the result of my own investigations, except as acknowledged.

Garching, July 18, 2008 .....

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Chapter 1

Introduction

Many-particle quantum mechanics gives – in its natural setting – rise to a Hamiltonian H which contains only single- and two-particle interactions (e.g., the Coulomb repulsion of electrons), although the number N of particles may be arbitrarily large. Consequently, the static energy of the system is completely determined by the two-body *reduced density matrix* (RDM) of the N-particle wavefunction Ψ (i.e., an *N-representable* density matrix). In mathematical terms,

$$\langle \Psi \,|\, H\Psi \rangle = \mathrm{tr}\left[h\Gamma_\Psi\right], \tag{1.1}$$

where h describes the two-body interaction and Γ_Ψ is the two-body reduced density matrix of Ψ. In case of fermions, the Pauli exclusion principle states that the total wavefunction must be antisymmetric – a key property contributing significantly to the degree of difficulty. Nevertheless, equation (1.1) states that the ground state of the system can be found by solving a linear programming problem on the set of N-representable two-body density matrices instead of a quadratic minimization problem on the full N-particle wavefunctions. This may open a door to escape the "curse of dimensionality" and motivates the *N-representability problem*:

Give a "practical" characterization of the set of two-body reduced density matrices which are N-representable.

Although reduced density matrices were extensively studied already fifty years ago by, for example, Yang (1962), Coleman (1963) and Löwdin (1955), new results have been obtained only very recently by Ruskai (2007) and Liu et al. (2007), who study the N-representability problem from a complexity class perspective, and Mazziotti (2007), who uses two-body reduced density matrices as key tool for the numeric solution of physical problems. Nevertheless, a complete analytic picture of the N-representability problem in the light of physically-motivated applications to, e.g., high-temperature superconductors, is still missing.

This work takes two approaches. In chapter 3, properties of fermionic reduced density matrices are investigated on a fairly abstract level, including a detailed analysis of one-body reduced density matrices (sections 3.3 and 3.4), the explicit determination of the two-body RDM eigenvalues for low dimensions (section 3.5) and pair structure inheritance (section 3.6).

In the second part of the thesis, we extend very recent work by Friesecke and Goddard (2008b,a) on the (non-relativistic, Born-Oppenheimer) many-particle

Schrödinger equation for atomic hull electrons in second-period atoms. The key lines of thought are as follows. Perturbation theory allows to project the full Schrödinger equation onto a finite-dimensional subspace of L^2 wavefunctions spanned by (dilated) Hydrogen orbitals. Most importantly, the well-known fact that the total angular momentum, spin and parity operators commute with the Hamiltonian still holds on the subspace which is invariant under these operators. Consequently, in order to block-diagonalize the Hamiltonian, one calculates the simultaneous eigenspaces of angular momentum, spin and parity, which is basically an algebraic problem *independent* of the Hamiltonian. The contribution of this thesis is as follows. Starting from ab initio calculations, we investigate the $3d$ vs. $4s$ orbital occupation in potassium, calcium and the transition metals scandium to zinc – which cannot be explained comprehensibly by semi-empirical chemists' models. To this end, we develop a *symbolic computation pipeline* automating the second-period calculations, since computation "by hand" becomes infeasible for higher dimensions. These efforts have resulted in an effective Coulomb integral solver using the computer algebra system Mathematica, and the Matlab toolbox FermiFab, which handles the fermionic RDM index mapping, incorporates the symbolic Coulomb integrals, performs numeric optimization and converts the results into human-readable form.

Chapter 2

Basic Concepts

We always assume that $\mathcal{H}$ is a finite-dimensional or separable Hilbert space. By $\wedge^N\mathcal{H}$ we denote the antisymmetrized N-fold tensor product (see Standard Example 27 in the appendix).

Definition 1. *Let $\Psi \in \wedge^N\mathcal{H}$, $\|\Psi\| = 1$, then its* p-body reduced density matrix *γ^p_Ψ $(1 \le p \le N)$ is a linear continuous operator $\wedge^p\mathcal{H} \to \wedge^p\mathcal{H}$ given by*

$$\langle \chi \,|\, \gamma^p_\Psi \varphi \rangle := \langle a_\varphi \Psi \,|\, a_\chi \Psi \rangle = \left\langle \Psi \,|\, a^\dagger_\varphi a_\chi \Psi \right\rangle \quad \forall\, \varphi, \chi \in \wedge^p\mathcal{H},$$

where $a^\dagger_\varphi$ and a_χ are the creation and annihilation operators of the states φ and χ, respectively. We denote the one- *and* two-body density matrices *by $\gamma_\Psi := \gamma^1_\Psi$ and $\Gamma_\Psi := \gamma^2_\Psi$.*

The integral version of the creation and annihilation operators for L^2 spaces (given in the appendix) allows us to identify γ^p_Ψ as an integral operator: for all $\varphi \in \wedge^p\mathcal{H}$,

$$\left(\gamma^p_\Psi \varphi\right)(x_1, \ldots, x_p) = \int_{\Omega^p} \gamma^p_\Psi(x_1, \ldots, x_p, x'_1, \ldots, x'_p)\, \varphi(x'_1, \ldots, x'_p)\, \mathrm{d}x'_1 \ldots\, \mathrm{d}x'_p$$

with the integral kernel (also denoted by γ^p_Ψ)

$$\begin{aligned}\gamma^p_\Psi(x_1, \ldots, x_p, &x'_1, \ldots, x'_p) := \\ &\binom{N}{p} \int_{\Omega^{N-p}} \Psi(x_1, \ldots, x_p, x_{p+1}, \ldots, x_N) \\ &\times \overline{\Psi(x'_1, \ldots, x'_p, x_{p+1}, \ldots, x_N)}\, \mathrm{d}x_{p+1} \ldots\, \mathrm{d}x_N.\end{aligned}$$

Thus we can state the following

Theorem 2. *γ^p_Ψ is compact, self-adjoint, nonnegative, trace class and has trace*

$$\operatorname{tr} \gamma^p_\Psi = \int_{\Omega^p} \gamma^p_\Psi(x_1, \ldots, x_p, x_1, \ldots, x_p)\, \mathrm{d}x_1 \ldots\, \mathrm{d}x_p = \binom{N}{p}.$$

Proof. γ^p_Ψ is positive semidefinite as

$$\langle \varphi \,|\, \gamma^p_\Psi \varphi \rangle = \|a_\varphi \Psi\|^2 \ge 0 \quad \forall \varphi \in \wedge^p\mathcal{H}.$$

The other assertions follow from the properties of integral operators given in the appendix. □

Assuming that the linear, self-adjoint Schrödinger operator H contains only one- and two-body interactions, it can be rewritten as

$$H = \sum_{\alpha<\beta} h_{\alpha,\beta}$$

for some $h : \wedge^2\mathcal{H} \to \wedge^2\mathcal{H}$. Given a complete orthonormal system $(\varphi_i)_i$ in $\wedge^2\mathcal{H}$, in terms of Second Quantization,

$$H = \sum_{i,j} \langle \varphi_i \,|\, h\varphi_j \rangle \, a^\dagger_{\varphi_i} a_{\varphi_j}.$$

Now we gain equation (1.1): for all normalized $\Psi \in \wedge^N\mathcal{H}$,

$$\begin{aligned}\langle \Psi \,|\, H\Psi \rangle &= \sum_{i,j} \langle \varphi_i \,|\, h\varphi_j \rangle \left\langle \Psi \,|\, a^\dagger_{\varphi_i} a_{\varphi_j} \Psi \right\rangle \\ &= \sum_{i,j} \langle \varphi_i \,|\, h\varphi_j \rangle \, \langle \varphi_j \,|\, \Gamma_\Psi \varphi_i \rangle \\ &= \sum_{i} \langle \varphi_i \,|\, h\Gamma_\Psi \varphi_i \rangle = \operatorname{tr}\left[h\Gamma_\Psi\right].\end{aligned}$$

An immediate consequence is the following formula for the ground state energy:

Proposition 3. *Let H be given as above, then*

$$\begin{aligned}\inf \operatorname{spec} H &= \inf\left\{ \langle \Psi \,|\, H\Psi \rangle \,:\, \Psi \in \wedge^N\mathcal{H},\, \|\Psi\| = 1 \right\} \\ &= \inf\left\{ \operatorname{tr}\left[h\Gamma_\Psi\right] \,:\, \Psi \in \wedge^N\mathcal{H},\, \|\Psi\| = 1 \right\},\end{aligned}$$

i.e. the ground state energy can be found by minimizing over the set of N-representable two-body density matrices.

Note that for the minimization problem, it is sufficient to characterize the set

$$\overline{\operatorname{conv}\left\{\Gamma_\Psi \,:\, \Psi \in \wedge^N\mathcal{H},\, \|\Psi\| = 1\right\}}^{\|\cdot\|_{\mathrm{tr}}}.$$

To illustrate the complexity reduction, let $K := \dim \mathcal{H} < \infty$ and compare the degrees of freedom:

$$\begin{aligned}\Gamma_\Psi \in \mathcal{B}\left(\wedge^2\mathcal{H}\right) &\simeq \mathbb{C}^{\binom{K}{2}\times\binom{K}{2}}, \quad \text{whereas} \\ \Psi \in \wedge^N\mathcal{H} &\simeq \mathbb{C}^{\binom{K}{N}}.\end{aligned}$$

Note that asymptotically for $1 \ll N \ll K$, one gets $\binom{K}{2}^2 \sim K^4$, but $\binom{K}{N} \sim K^N$.

Finally, we connect reduced density matrices to quantum channels[1], a well-known concept studied in quantum information theory. In the formalism of second quantization, the p-body reduced density matrix γ^p_Ψ of a fermionic N-body pure state Ψ can be written as

$$\gamma^p_\Psi = \operatorname{tr}_{p+1,\ldots,N} |\Psi\rangle\langle\Psi| = \sum_{i_{p+1}<\cdots<i_N} a_{|i_{p+1},\ldots,i_N\rangle} \, |\Psi\rangle\langle\Psi| \, a^\dagger_{|i_{p+1},\ldots,i_N\rangle}.$$

[1] For an introduction, refer to Nielsen and Chuang (2000).

By a linear extension to density matrices on $\wedge^N \mathcal{H}$, we get a completely positive, (up to the normalization factor $\binom{N}{p}$) trace preserving *quantum channel*

$$\gamma^p : \mathcal{B}\left(\wedge^N \mathcal{H}\right) \to \mathcal{B}\left(\wedge^p \mathcal{H}\right)$$

with Kraus operators $a_{|i_{p+1},\ldots,i_N\rangle}$ for all $1 \leq i_{p+1} < \cdots < i_N \leq \dim \mathcal{H}$.

Chapter 3

Properties of Fermion Density Matrices

3.1 General characteristics

By the Hilbert Schmidt theorem, there is a complete orthonormal system $(\varphi_i)_i$ in $\wedge^p\mathcal{H}$ of eigenvectors of γ_Ψ^p, i.e.

$$\gamma_\Psi^p\varphi_i = \lambda_i\varphi_i, \quad \lambda_i \in \mathbb{R} \qquad \text{for all } i.$$

Consider the one-body case $p = 1$. By Standard Example 27 in the appendix, Ψ can be expanded in $(\varphi_{i_1} \wedge \cdots \wedge \varphi_{i_N})_{i_1<\cdots<i_N}$. The following proposition shows that it is sufficient to consider eigenvectors with nonzero eigenvalues only, which will be particularly interesting if $\operatorname{rank}\gamma_\Psi < \infty$.

Proposition 4. *Ψ can be expanded as a linear combination of Slater determinants constructed from eigenvectors of γ_Ψ which belong to nonzero eigenvalues.*

Proof. What remains to be shown is the following: if $\gamma_\Psi\varphi_i = 0$, φ_i won't show up in the expansion:

$$\|a_{\varphi_i}\Psi\|^2 = \langle\varphi_i \,|\, \gamma_\Psi\varphi_i\rangle = 0.$$

□

Note that γ_Ψ^p contains less information the smaller p gets, or more strictly speaking:

Proposition 5. *Let $\Psi \in \wedge^N\mathcal{H}$, $\|\Psi\| = 1$, then γ_Ψ^p can be obtained from γ_Ψ^{p+1}.*

Proof. For any complete orthonormal system $|i\rangle_i$ of $\mathcal{H}$,

$$\begin{aligned}
&\sum_k \left\langle i_1 \wedge \cdots \wedge i_p \wedge k \,|\, \gamma_\Psi^{p+1}\, j_1 \wedge \cdots \wedge j_p \wedge k \right\rangle \\
&= \left\langle \Psi \,|\, a_{j_1}^\dagger \cdots a_{j_p}^\dagger \left(\sum_k \hat{n}_k\right) a_{i_p} \cdots a_{i_1}\Psi \right\rangle \\
&= (N-p)\,\langle i_1 \wedge \cdots \wedge i_p \,|\, \gamma_\Psi^p\, j_1 \wedge \cdots \wedge j_p\rangle\,.
\end{aligned}$$

□

Proposition 6. *Let $\Psi := \psi_1 \wedge \cdots \wedge \psi_N$ be a Slater determinant with orthonormal $\psi_1, \ldots, \psi_N \in \mathcal{H}$. Then γ_Ψ^p is the orthogonal projection on the subspace spanned by $\left(\psi_{i_1} \wedge \cdots \wedge \psi_{i_p}\right)_{i_1 < \cdots < i_p}$.*

This can be seen by an explicit calculation or derived directly from the definition of γ_Ψ^p using creation and annihilation operators.

It is currently not known whether the converse is also true, except for $p = 1$:

Proposition 7. *Ψ is a Slater determinant if and only if γ_Ψ is an orthogonal projection.*

Proof. Only "$\Leftarrow$" remains to be shown. From $\sigma(\gamma_\Psi) = \{0, 1\}$ and $\operatorname{tr} \gamma_\Psi = N$ it follows that $\operatorname{rank} \gamma_\Psi = N$. That is, by proposition 4, Ψ can be expanded into a single Slater determinant. □

We make use of the anticommutator relations for creation and annihilation operators to show the following proposition, which is intricately connected with the antisymmetry constraint of the wave function.

Proposition 8. *The expected values of γ_Ψ are in the range $[0, 1]$.*

Proof. We have already shown that γ_Ψ is positive semidefinite. $\gamma_\Psi \leq 1$ follows from

$$\langle \varphi \,|\, \gamma_\Psi \varphi \rangle = \left\langle \Psi \,|\, a_\varphi^\dagger a_\varphi \Psi \right\rangle = \left\langle \Psi \,|\, \left(1 - a_\varphi a_\varphi^\dagger\right) \Psi \right\rangle = \|\Psi\|^2 - \left\| a_\varphi^\dagger \Psi \right\|^2 \leq 1.$$

□

We state a classification of the ranks of fermion one-body density matrices. A proof has been given by Friesecke (2003).

Theorem 9. *There exists a $\Psi \in \wedge^N \mathcal{H}$ such that $\operatorname{rank} \gamma_\Psi = K$, if and only if*

$$K = \begin{cases} 1 & N = 1 \\ \geq 2, \ \textit{even} & N = 2 \\ \geq N, \neq N + 1 & N \geq 3 \end{cases}$$

In particular, $\operatorname{rank} \gamma_\Psi$ is at least N and cannot be equal to $N + 1$.

Given an unitary operator $U : \mathcal{H} \to \mathcal{H}$, we obtain an unitary operator (also denoted by U) acting on $\wedge^N \mathcal{H}$ by

$$U(i_1 \wedge \cdots \wedge i_N) := (Ui_1) \wedge \cdots \wedge (Ui_N).$$

Proposition 10. *Given such an unitary operator U,*

$$U^* \gamma_{U\Psi}^p U = \gamma_\Psi^p.$$

Proof. We use

$$U^* a^\dagger_{U\varphi} U = a^\dagger_\varphi, \quad U^* a_{U\varphi} U = a^\dagger_\varphi \qquad \text{for all } \varphi \in \wedge^N \mathcal{H}$$

to get

$$\begin{aligned}\langle \chi \,|\, U^* \gamma^p_{U\Psi} U\varphi \rangle &= \left\langle U\Psi \,|\, a^\dagger_{U\varphi} a_{U\chi} U\Psi \right\rangle = \left\langle \Psi \,|\, \left(U^* a^\dagger_{U\varphi} U\right)\left(U^* a_{U\chi} U\right)\Psi \right\rangle \\ &= \left\langle \Psi \,|\, a^\dagger_\varphi a_\chi \Psi \right\rangle = \langle \chi \,|\, \gamma^p_\Psi \varphi \rangle \quad \text{for all } \varphi, \chi \in \wedge^p \mathcal{H}.\end{aligned}$$

□

This might be a starting point for a simplification of the problem: introduce equivalence classes on $\wedge^N \mathcal{H}$ by $\Psi \sim \Phi :\Leftrightarrow \Psi = U\Phi$ for some unitary U.

As an immediate consequence of proposition 10, the convex hull

$$\operatorname{conv}\left\{\gamma^p_\Psi \,:\, \Psi \in \wedge^N \mathcal{H}, \|\Psi\| = 1\right\}$$

is invariant under these unitary transformations, since

$$U^* \left(\sum_{i=1}^n \alpha_i \gamma^p_{\Psi_i}\right) U = \sum_{i=1}^n \alpha_i \gamma^p_{U^*\Psi_i}$$

for all $0 \le \alpha_1, \ldots, \alpha_n \le 1$ with $\alpha_1 + \cdots + \alpha_n = 1$.

3.2 Duality between γ^p_Ψ and γ^{N-p}_Ψ

We may further expand the concept of the annihilation operator: define an antilinear operator

$$\hat{\Psi} : \wedge^p \mathcal{H} \to \wedge^{N-p} \mathcal{H}, \quad (\hat{\Psi}\varphi)(x) := (a_\varphi \Psi)(x) = \binom{N}{p}^{\frac{1}{2}} \int_{\Omega^p} \overline{\varphi(y)} \Psi(y, x)\, \mathrm{d}y,$$

where $x \in \Omega^{N-p}$ and y runs over all Ω^p. Note that for all $\varphi \in \wedge^p \mathcal{H}$ and $\chi \in \wedge^{N-p} \mathcal{H}$,

$$\begin{aligned}\left\langle \chi \,|\, \hat{\Psi}\varphi \right\rangle &= \binom{N}{p}^{\frac{1}{2}} \int_{\Omega^N} \overline{\chi(x)\varphi(y)} \Psi(y, x)\, \mathrm{d}x\, \mathrm{d}y \\ &= (-1)^{(N-p)\,p} \binom{N}{p}^{\frac{1}{2}} \int_{\Omega^N} \overline{\varphi(y)\chi(x)} \Psi(x, y)\, \mathrm{d}x\, \mathrm{d}y \\ &= (-1)^{(N-p)\,p} \left\langle \varphi \,|\, \hat{\Psi}\chi \right\rangle,\end{aligned}$$

where the sign factor comes from the permutation $(y, x) \to (x, y)$. Using this property, it follows that

$$\langle \chi \,|\, \gamma^p_\Psi \varphi \rangle = \langle a_\varphi \Psi \,|\, a_\chi \Psi \rangle = \left\langle \hat{\Psi}\varphi \,|\, \hat{\Psi}\chi \right\rangle = (-1)^{(N-p)\,p} \left\langle \chi \,|\, \hat{\Psi}^2 \varphi \right\rangle$$

for all $\varphi, \chi \in \wedge^p \mathcal{H}$, i.e.

$$\gamma^p_\Psi = (-1)^{(N-p)\,p}\, \hat{\Psi}^2.$$

Proposition 11. *There is a one-to-one correspondence between the normalized eigenvectors of γ_Ψ^p and γ_Ψ^{N-p} with the same nonzero eigenvalue.*

Proof. Let

$$\gamma_\Psi^p \varphi = \lambda\varphi, \quad \lambda > 0, \quad \varphi \in \wedge^p\mathcal{H} \text{ with } \|\varphi\| = 1.$$

Define

$$\chi := \frac{i^{(N-p)\,p}}{\sqrt{\lambda}} \hat{\Psi}\varphi,$$

then $\|\chi\| = 1$ as

$$\left\|\hat{\Psi}\varphi\right\|^2 = \|a_\varphi \Psi\|^2 = \langle \varphi \,|\, \gamma_\Psi^p \varphi\rangle = \lambda \langle \varphi \,|\, \varphi\rangle$$

and χ is an eigenvector of γ_Ψ^{N-p} with eigenvalue λ. In fact,

$$\gamma_\Psi^{N-p}\left(\hat{\Psi}\varphi\right) = (-1)^{(N-p)\,p}\hat{\Psi}^3\varphi = \hat{\Psi}\gamma_\Psi^p\varphi = \lambda\left(\hat{\Psi}\varphi\right).$$

Applying the same rule to χ, we recover the original φ:

$$\frac{i^{p\,(N-p)}}{\sqrt{\lambda}}\hat{\Psi}\chi = \frac{(-1)^{p\,(N-p)}}{\lambda}\hat{\Psi}^2\varphi = \frac{1}{\lambda}\gamma_\Psi^p\varphi = \varphi.$$

If $\varphi' \in \wedge^p\mathcal{H}$ is another normalized eigenvector of λ perpendicular to φ, then χ' is perpendicular to χ:

$$\langle \chi' \,|\, \chi\rangle = \frac{1}{\lambda}\left\langle \hat{\Psi}\varphi' \,|\, \hat{\Psi}\varphi\right\rangle = \frac{1}{\lambda}\langle \varphi \,|\, \gamma_\Psi^p\varphi'\rangle = \langle \varphi \,|\, \varphi'\rangle = 0.$$

Note that γ_Ψ^p is Hilbert-Schmidt, hence all nonzero eigenvalues have finite multiplicity and eigenvectors corresponding to different eigenvalues are orthogonal. □

3.3 Decomposition of the one-body density matrix

We first derive a formula due to Ando (1963). Let $|i\rangle_i$ be a complete orthonormal system of eigenvectors of γ_Ψ with corresponding eigenvalues λ_i such that λ_1 is the greatest eigenvalue. Ψ can be expanded in Slater determinants as follows:

$$\Psi = \sum_{\substack{I=(i_1,\ldots,i_N)\\ i_1<\cdots<i_N}} x_I\,|i_1,\ldots,i_N\rangle, \quad x_I \in \mathbb{C}.$$

Set

$$\Phi_a := \sum_{1\in I} x_I\,|i_2,\ldots,i_N\rangle \in \wedge^{N-1}\mathcal{H} \quad \text{and}$$
$$\Phi_b := \sum_{1\notin I} x_I\,|i_1,\ldots,i_N\rangle \in \wedge^N\mathcal{H},$$

then $\Psi = a_1^\dagger \Phi_a + \Phi_b$. From that,

$$\begin{aligned}\langle i \,|\, \gamma_\Psi j\rangle = \left\langle \Psi \,|\, a_j^\dagger a_i \Psi \right\rangle &= \left\langle \Phi_a \,|\, a_1 a_j^\dagger a_i a_1^\dagger \Phi_a \right\rangle \\ &+ \left\langle \Phi_b \,|\, a_j^\dagger a_i a_1^\dagger \Phi_a \right\rangle + \left\langle \Phi_a \,|\, a_1 a_j^\dagger a_i \Phi_b \right\rangle + \left\langle \Phi_b \,|\, a_j^\dagger a_i \Phi_b \right\rangle .\end{aligned}$$

Since $a_1 \Phi_a = 0$, the first term equals

$$\left\langle \Phi_a \,|\, a_1 a_j^\dagger a_i a_1^\dagger \Phi_a \right\rangle = \|\Phi_a\|^2 \langle i \,|\, 1\rangle \langle 1 \,|\, j\rangle + \left\langle \Phi_a \,|\, a_j^\dagger a_i \Phi_a \right\rangle ,$$

and

$$\|\Phi_a\|^2 = \langle 1 \,|\, \gamma_\Psi 1\rangle = \lambda_1 .$$

Iff $\Phi_b = 0$, we have $\lambda_1 = \|\Phi_a\|^2 = \|\Psi\|^2 = 1$; then

$$\gamma_\Psi = |1\rangle\langle 1| + \gamma_{\Phi_a} .$$

Now, let $\lambda_1 \neq 1$, i.e. $\lambda_1 < 1$.

Clearly, $\left\langle \Phi_a \,|\, a_1 a_j^\dagger a_i \Phi_b \right\rangle$ is zero for $i = 1$ and $i, j \neq 1$. In the remaining case $i \neq 1, j = 1$ it equals $\langle i \,|\, \gamma_\Psi 1\rangle = 0$, i.e. it vanishes altogether. Note that this implies the total orthogonality of Φ_a and Φ_b, $\langle \Phi_a \,|\, a_i \Phi_b\rangle = 0$ for all i. An analogous argument shows that $\left\langle \Phi_b \,|\, a_j^\dagger a_i a_1^\dagger \Phi_a \right\rangle = 0$ for all i, j.

Set

$$\Psi_a := \frac{\Phi_a}{\|\Phi_a\|} \quad \text{and} \quad \Psi_b := \frac{\Phi_b}{\|\Phi_b\|},$$

then the decomposition can be written as

$$\langle i \,|\, \gamma_\Psi j\rangle = \lambda_1 \langle i \,|\, 1\rangle \langle 1 \,|\, j\rangle + \lambda_1 \langle i \,|\, \gamma_{\Psi_a} j\rangle + \|\Phi_b\|^2 \langle i \,|\, \gamma_{\Psi_b} j\rangle .$$

Using

$$N = \operatorname{tr} \gamma_\Psi = \sum_i \langle i \,|\, \gamma_\Psi i\rangle = \lambda_1 + \lambda_1 (N-1) + N \|\Phi_b\|^2 ,$$

we get $\|\Phi_b\|^2 = 1 - \lambda_1$. Summarising finally yields

Lemma 12. *γ_Ψ can be decomposed into*

$$\gamma_\Psi = \lambda_1 |1\rangle\langle 1| + \lambda_1 \gamma_{\Psi_a} + (1 - \lambda_1)\, \gamma_{\Psi_b}, \tag{3.1}$$

where $\Psi_a \in \wedge^{N-1}\mathcal{H}$ and $\Psi_b \in \wedge^N \mathcal{H}$ are normalized functions such that

$$\begin{gathered}\Psi = \sqrt{\lambda_1} \cdot a_1^\dagger \Psi_a + \sqrt{1 - \lambda_1} \cdot \Psi_b \quad \textit{and} \\ a_1 \Psi_a = 0, \quad a_1 \Psi_b = 0, \quad \langle \Psi_a \,|\, a_i \Psi_b\rangle = 0 \quad \forall\, i.\end{gathered}$$

In the following we need another lemma which can be found in Ando (1963).

Lemma 13. *In the decomposition* (3.1)*, if γ_{Ψ_a} has a normalized eigenvector φ belonging to the eigenvalue* 1*, then φ will also be an eigenvector of γ_Ψ belonging to the eigenvalue λ_1, and $a_\varphi \Psi_b = 0$ when $\lambda_1 \neq 1$.*

Proof. Since λ_1 is the greatest eigenvalue of γ_Ψ, the assertion follows from

$$\lambda_1 \geq \langle \varphi \,|\, \gamma_\Psi \varphi \rangle = \lambda_1 \left| \langle 1 \,|\, \varphi \rangle \right|^2 + \lambda_1 \underbrace{\langle \varphi \,|\, \gamma_{\Psi_a} \varphi \rangle}_{=1} + (1 - \lambda_1) \langle \varphi \,|\, \gamma_{\Psi_b} \varphi \rangle \geq \lambda_1.$$

□

Now we can proof a slightly sharper form of a result due to Ando (1963). Proposition 7 handles the case $\operatorname{rank} \gamma_\Psi = N$, and $\operatorname{rank} \gamma_\Psi$ can never be $N + 1$, by theorem 9. The next simplest step is therefore rank $N + 2$.

Proposition 14. *Let* $\operatorname{rank} \gamma_\Psi = N + 2$. *Then,*

- *if N is odd, $\lambda_1 = 1$ and each of the remaining nonzero eigenvalues will be evenly degenerate,*
- *if N is even, each nonzero eigenvalue will be evenly degenerate.*

Let $\{\varphi_1, \ldots, \varphi_{N+2}\}$ be the set of orthonormal eigenvectors of γ_Ψ corresponding to nonzero eigenvalues $\lambda_1, \ldots, \lambda_{N+2}$, respectively. Then Ψ is a linear combination of, at most, $\frac{N+1}{2}$ (N odd) or $\frac{N}{2} + 1$ (N even) Slater determinants constructed from these eigenvectors.

Proof. If $N = 1$, $\operatorname{rank} \gamma_\Psi$ cannot $N + 2$ by theorem 9. If $N = 2$, in the decomposition 3.1, $\Psi_a =: \varphi_2 \in \mathcal{H}$ is a function of a single particle. Using lemma 13,

$$\gamma_\Psi = \lambda_1 |\varphi_1\rangle\langle\varphi_1| + \lambda_1 |\varphi_2\rangle\langle\varphi_2| + (1 - \lambda_1)\, \gamma_{\Psi_b},$$

and thus $\lambda_1 < 1$ is at least doubly degenerate. Since $\operatorname{rank} \gamma_{\Psi_b}$ must be equal to 2, Ψ_b is a Slater determinant: $\Psi_b = \varphi_3 \wedge \varphi_4$ with orthonormal $\varphi_1, \ldots, \varphi_4$. Finally,

$$\Psi = \sqrt{\lambda_1} \cdot \varphi_1 \wedge \varphi_2 + \sqrt{1 - \lambda_1} \cdot \varphi_3 \wedge \varphi_4$$

is a linear combination of 2 Slater determinants, as required. For general N, consider again the decomposition (3.1):

$$\gamma_\Psi = \lambda_1 |\varphi_1\rangle\langle\varphi_1| + \lambda_1 \gamma_{\Psi_a} + (1 - \lambda_1)\, \gamma_{\Psi_b}.$$

The case $\lambda_1 = 1$: then the last term vanishes, and since $a_{\varphi_1} \Psi_a = 0$, every eigenvector of γ_{Ψ_a} is also an eigenvector of γ_Ψ with the same eigenvalue. From $\operatorname{rank} \gamma_{\Psi_a} = N + 1$ we gain the assertion by induction. Note that $\Psi = a^\dagger_{\varphi_1} \Psi_a$, hence the number of Slater determinants in the expansion of Ψ and Ψ_a is the same.

The case $\lambda_1 < 1$: we have $\operatorname{rank} \gamma_{\Psi_b} \leq N + 1$ as $\operatorname{rank} \gamma_\Psi \geq 1 + \operatorname{rank} \gamma_{\Psi_b}$. (Note that γ_{Ψ_a} and γ_{Ψ_b} are positive semidefinite.) By theorem 9, $\operatorname{rank} \gamma_{\Psi_b} \neq N + 1$, hence $\operatorname{rank} \gamma_{\Psi_b} = N$ and Ψ_b is a Slater determinant. Thus, there are orthonormal $\psi_1, \ldots, \psi_N \in \mathcal{H}$ such that $\Psi_b = \psi_1 \wedge \cdots \wedge \psi_N$, and γ_{Ψ_b} is an orthogonal projection on the subspace spanned by $\psi_1, \ldots, \psi_N$.

We show next that, on the contrary, Ψ_a cannot be a Slater determinant: assuming $\Psi_a = \chi_2 \wedge \cdots \wedge \chi_N$, each χ_i is an eigenvector of γ_{Ψ_a} with eigenvalue 1; thus by lemma 13, it is also an eigenvector of γ_Ψ, and $\langle \chi_i \,|\, \psi_j \rangle = 0$ for all i, j. This means that $\operatorname{rank} \gamma_\Psi = 2N$, contradicting the assumptions if $N \geq 3$.

In the sole remaining case $\operatorname{rank}\gamma_{\Psi_a} = N+1$, the range of γ_{Ψ_a} must be spanned by $\psi_1, \ldots, \psi_N$ and one more additional vector, denoted ψ_{N+1}. Hence Ψ_a can be written as

$$\Psi_a = \sum_{1 \le i_1 < \cdots < i_{N-1} \le N+1} x_{i_1,\ldots,i_{N-1}} \cdot \psi_{i_1} \wedge \cdots \wedge \psi_{i_{N-1}}.$$

By 3.1, for all $i = 1 \ldots N$, $x_{1,\ldots,i-1,i+1,\ldots,N} = \langle \Psi_a \,|\, a_{\psi_i} \Psi_b \rangle = 0$, i.e. only configurations with $i_{N-1} = N+1$ contribute to the sum. Thus ψ_{N+1} is an eigenvector of γ_{Ψ_a} with eigenvalue 1, and - by lemma 13 - also an eigenvector of γ_Ψ. Without loss of generality we may assume $\varphi_2 = \psi_{N+1}$.

Applying the decomposition 3.1 to Ψ_a yields

$$\gamma_{\Psi_a} = |\varphi_2\rangle\langle\varphi_2| + \gamma_\Phi,$$

where $\Phi \in \wedge^{N-2}\mathcal{H}$ and $\operatorname{rank}\gamma_\Phi = N$. Let $\chi_1, \ldots, \chi_N$ be the normalized eigenvectors of γ_Φ belonging to nonzero eigenvalues $\mu_1, \ldots, \mu_N$, respectively. Since these eigenvectors span the same subspace as $\{\psi_1, \ldots, \psi_N\}$, we have $\gamma_{\Psi_b} = \sum_{i=1}^N |\chi_i\rangle\langle\chi_i|$, and without loss of generality, $\Psi_b = \chi_1 \wedge \cdots \wedge \chi_N$.

Putting everything together, it follows that

$$\gamma_\Psi = \lambda_1 |\varphi_1\rangle\langle\varphi_1| + \lambda_1 |\varphi_2\rangle\langle\varphi_2| + \sum_{i=1}^N (\lambda_1 \mu_i + 1 - \lambda_1)\, |\chi_i\rangle\langle\chi_i|.$$

Thus we have identified the χ_i's as eigenvectors of γ_Ψ, that is, without loss of generality, $\varphi_{i+2} = \chi_i$ for all $i = 1 \ldots N$. N cannot be odd, since otherwise, by induction, $\mu_1 = 1$ and φ_3 was an eigenvector of γ_Ψ with eigenvalue 1, contradicting $\lambda_1 < 1$. But N being even, each μ_i is evenly degenerate and hence also the eigenvalues of γ_Ψ. Note that

$$\Psi = a^\dagger_{\varphi_1} \Psi_a + \Psi_b = a^\dagger_{\varphi_1} \Psi_a + \Psi_b = a^\dagger_{\varphi_1} a^\dagger_{\varphi_2} \Phi + \varphi_3 \wedge \cdots \wedge \varphi_{N+2}.$$

Since the eigenvectors $\chi_1, \ldots, \chi_N$ of γ_Φ are also eigenvectors of γ_Ψ, the asserted expansion of Ψ follows by induction. □

A generalization of the assertion for the case $N = 2$ in proposition 14 can be found in Friesecke (2003):

Proposition 15. *Let $\Psi \in \wedge^N \mathcal{H}$, $\|\Psi\| = 1$. If $N \equiv 2 \mod 4$, then each nonzero eigenvalue of $\gamma_\Psi^{N/2}$ is evenly degenerate.*

The proof uses the self-duality of $\gamma_\Psi^{N/2}$.

3.4 The convex hull of one-body density matrices

It is a well known fact in physics that the ground states of non-interacting many particle systems are Slater determinants. In this section we present a rigorous mathematical proof that Slater determinants actually are the extreme points of the set of one-body density matrices.

Let $\mathcal{H}$ be a separable Hilbert space. For every trace class $A : \mathcal{H} \to \mathcal{H}$ with

$$A\varphi = \sum_{i=1}^\infty \lambda_i \langle \varphi_i \,|\, \varphi \rangle \, \varphi_i \quad \forall \varphi \in \mathcal{H}, \quad \langle \varphi_i \,|\, \varphi_j \rangle = \delta_{ij}, \quad \lambda_i \in \mathbb{R},$$

the trace norm equals

$$\|A\|_{\mathrm{tr}} = \sum_{i=1}^{\infty} |\lambda_i| \,. \tag{3.2}$$

Theorem 16. *Given a separable Hilbert space $\mathcal{H}$,*

$$\begin{aligned}&\overline{\operatorname{conv}\left\{\gamma_\Psi \,:\, \Psi \in \wedge^N\mathcal{H}, \|\Psi\| = 1\right\}}^{\|\cdot\|_{\mathrm{tr}}} \\ &= \left\{g : \mathcal{H} \to \mathcal{H} \,:\, g \text{ selfadjoint}, 0 \le g \le 1, \operatorname{tr} g = N\right\}.\end{aligned}$$

Designate the left set by L and the right set by R. Note that every $g \in R$ is trace class and hence compact.

Proof.

- "$\subseteq$" follows from $\gamma_\Psi \in R$ for all Ψ as well as R convex and closed with respect to $\|\cdot\|_{\mathrm{tr}}$ since $\|A\| \le \|A\|_{\mathrm{tr}}$ for all $A : \mathcal{H} \to \mathcal{H}$ trace class.

- "$\supseteq$" According to the Hilbert-Schmidt theory for compact self-adjoint operators, every $g \in R$ has a complete orthonormal system $(\varphi_i)_{i\in\mathbb{N}}$ of eigenvectors with corresponding eigenvalues $\lambda_i \in \mathbb{R}$, i.e.

  $$g\varphi = \sum_{i=1}^{\infty} \lambda_i \langle \varphi_i \,|\, \varphi\rangle \, \varphi_i \quad \forall \varphi \in \mathcal{H}.$$

  We have $0 \le \lambda_i \le 1$ and $\sum_i \lambda_i = \operatorname{tr} g = N$. If $\Psi = \varphi_{i_1} \wedge \cdots \wedge \varphi_{i_N}$ is a Slater determinant, then

  $$\gamma_\Psi \varphi = \sum_{k=1}^{N} \langle \varphi_{i_k} \,|\, \varphi\rangle \, \varphi_{i_k} \quad \forall \varphi \in \mathcal{H}.$$

  The assertion follows now from (3.2) and the following lemma.

□

Remember that

$$\ell^1 := \left\{ (t_n) \,:\, t_n \in \mathbb{R} \ \forall n \in \mathbb{N}, \sum_{n=1}^{\infty} |t_n| < \infty \right\}$$

is a Banach space over $\mathbb{R}$ with the norm

$$\|t\|_1 := \sum_{n=1}^{\infty} |t_n| \,.$$

Lemma 17. *Let*

$$T := \left\{ t \in \ell^1 \,:\, 0 \le t_n \le 1 \ \forall n, \|t\|_1 = N \right\} \subset \ell^1,$$

then the extreme points are

$$\operatorname{ex} T = \{t \in T \,:\, t_n \in \{0, 1\} \ \forall n\}$$

and

$$T = \overline{\operatorname{conv} \operatorname{ex} T}.$$

Proof. Let $t \in T$ and $0 < t_i < 1$ for an $i \in \mathbb{N}$. Since $\|t\|_1 = N \in \mathbb{N}$, there is an $j \neq i$ such that $0 < t_j < 1$. For $\epsilon > 0$ small enough,

$$\begin{aligned} r &:= (t_1, t_2, \dots, t_i + \epsilon, \dots, t_j - \epsilon, \dots) \in T \quad \text{and} \\ s &:= (t_1, t_2, \dots, t_i - \epsilon, \dots, t_j + \epsilon, \dots) \in T. \end{aligned}$$

As $t = \frac{1}{2}(r + s)$, $t \notin \operatorname{ex} T$.

Now let $t \in T$, $t_n \in \{0, 1\}$ $\forall n$. From $t = \frac{1}{2}(x + y)$ with $x, y \in T$ it follows that $x = y = t$, i.e. $t \in \operatorname{ex} T$.

We show next, by induction with respect to m, that

$$t \in \operatorname{conv} \operatorname{ex} T \quad \forall\, t \in T \text{ with } t_n = 0\ \forall n > m, \quad m \in \mathbb{N} \text{ fixed.}$$

$m = N$: then $t \in \operatorname{ex} T$.
$m = N + 1$: set

$$s_n^i := \begin{cases} 1 & n \neq i, 1 \leq n \leq N+1 \\ 0 & \text{otherwise} \end{cases}, \quad i = 1, \dots, N+1.$$

Then $s^i \in \operatorname{ex} T$ and $t = \sum_{i=1}^{N+1} (1 - t_i)\, s^i$.
$m > N + 1$: without loss of generality $t_m \neq 0$ and $t_n \geq t_m$ $\forall n = 1, \dots, m$. Set

$$s_n := \begin{cases} 1 & m - N < n \leq m \\ 0 & \text{otherwise} \end{cases}$$

and

$$r := \frac{1}{1 - t_m} [t - t_m s] \in T.$$

By induction, $r \in \operatorname{conv} \operatorname{ex} T$, hence also

$$t = (1 - t_m) r + t_m s \in \operatorname{conv} \operatorname{ex} T.$$

Finally, let $t \in T$. Given $\epsilon > 0$, choose $m \in \mathbb{N}$ with $\sum_{n>m} |t_n| < \frac{\epsilon}{2}$. Without loss of generality $t_m \leq 1 - \frac{\epsilon}{2}$. Set

$$r_n := \begin{cases} t_n & n < m \\ t_m + \sum_{k>m} t_k & n = m \\ 0 & n > m \end{cases},$$

then $r \in \operatorname{conv} \operatorname{ex} T$ by the above result and $\|t - r\|_1 < \epsilon$. □

3.5 Eigenvalues of Γ_Ψ in case of even $K = N + 2$

Let again $\mathcal{H}$ be a finite, K-dimensional Hilbert space and $\Psi \in \wedge^N \mathcal{H}$ an N-particle antisymmetrized wavefunction, and additionally assume that $K = N+2$ and N is even. We remark that the former is equivalent to demanding $\operatorname{rank} \gamma_\Psi \leq N + 2$ as Ψ can always be expanded in eigenvectors of γ_Ψ corresponding to nonzero eigenvalues.[1] By duality, there exists a $\varphi \in \wedge^2 \mathcal{H}$ such that

$$\Psi = a_\varphi |12 \dots K\rangle,$$

[1] Also compare with proposition 14.

and – since we are interested in the eigenvalues of Γ_Ψ – by the Coleman expansion theorem we may w.l.o.g. express $\varphi = \sum_{i=1}^{K/2} \overline{x_i}|2i-1, 2i\rangle$ with $x_i \in \mathbb{C}$. Then

$$\Psi = \sum_{i=1}^{K/2} x_i \cdot a_{2i}\, a_{2i-1}|12\dots K\rangle, \quad \sum_i |x_i|^2 = 1$$

as shown in figure 3.1 for a single Slater determinant. Note that $\{|1\rangle, \dots, |K\rangle\}$

Figure 3.1: Illustration of $a_{|2i-1,2i\rangle}|12\dots K\rangle$

are exactly the eigenvalues of the 1-particle reduced density matrix γ_Ψ as

$$\langle i\,|\,\gamma_\Psi j\rangle = \langle a_j\Psi\,|\,a_i\Psi\rangle = \delta_{ij}\left(1 - |x_k|^2\right) \quad \text{with} \quad i \in \{2k-1, 2k\}.$$

A direct inspection shows that

$$\langle ij\,|\,\Gamma_\Psi\, ij\rangle = \|a_j a_i \Psi\|^2 = \sum_{\substack{k \\ \{2k-1,2k\} \\ \cap\{i,j\}=\emptyset}} |x_k|^2 = 1 - \sum_{\substack{k \\ \{2k-1,2k\} \\ \cap\{i,j\}\neq\emptyset}} |x_k|^2$$

and for $|ij\rangle \neq |pq\rangle$

$$\langle pq\,|\,\Gamma_\Psi\, ij\rangle = \begin{cases} \overline{x_l} \cdot x_k, & |ij\rangle = |2k-1, 2k\rangle \text{ and } |pq\rangle = |2l-1, 2l\rangle \\ 0, & \text{otherwise} \end{cases}$$

Note that all $|ij\rangle$ which cannot be written as $|ij\rangle = |2k-1, 2k\rangle$ are eigenvectors of Γ_Ψ with corresponding eigenvalue zero, so it only remains to determine the eigenvalues of the submatrix

$$G^n_\Psi := \begin{pmatrix} 1-|x_1|^2 & \overline{x_1}\cdot x_2 & \dots & \overline{x_1}\cdot x_n \\ \overline{x_2}\cdot x_1 & 1-|x_2|^2 & & \vdots \\ \vdots & & \ddots & \\ \overline{x_n}\cdot x_1 & \dots & & 1-|x_n|^2 \end{pmatrix}, \quad n = K/2. \tag{3.3}$$

For example, in case of $K = 6$, we have $\varphi = \overline{x_1}\,|12\rangle + \overline{x_2}\,|34\rangle + \overline{x_3}\,|56\rangle$, so

$$\Psi = a_\varphi|123456\rangle = x_1|3456\rangle + x_2|1256\rangle + x_3|1234\rangle.$$

Then $a_{|2i-1,2i\rangle}\Psi$ is explicitly

$$\begin{aligned} a_{|12\rangle}\Psi &= x_2|56\rangle + x_3|34\rangle, \\ a_{|34\rangle}\Psi &= x_1|56\rangle + x_3|12\rangle, \\ a_{|56\rangle}\Psi &= x_1|34\rangle + x_2|12\rangle \end{aligned}$$

and $a_{|13\rangle}\Psi = -x_3|24\rangle$, $a_{|14\rangle}\Psi = x_3|23\rangle, \ldots$. Plugging these in yields

$$\begin{aligned}
\langle 12\,|\,\Gamma_\Psi\,12\rangle &= \left\|a_{|12\rangle}\Psi\right\|^2 = |x_2|^2 + |x_3|^2 = 1 - |x_1|^2\,,\\
\langle 34\,|\,\Gamma_\Psi\,12\rangle &= \left\langle a_{|12\rangle}\Psi\,|\,a_{|34\rangle}\Psi\right\rangle = \overline{x_2}\cdot x_1,\\
\langle 13\,|\,\Gamma_\Psi\,12\rangle &= \left\langle a_{|12\rangle}\Psi\,|\,a_{|13\rangle}\Psi\right\rangle = 0,\\
\langle 13\,|\,\Gamma_\Psi\,13\rangle &= \left\|a_{|13\rangle}\Psi\right\|^2 = |x_3|^2\,,\\
&\vdots
\end{aligned}$$

Expressed in the basis set $B \cup C_1 \cup C_2 \cup C_3$ with

$$\begin{aligned}
B &= (|12\rangle, |34\rangle, |56\rangle)\\
C_1 &= (|35\rangle, |36\rangle, |45\rangle, |46\rangle)\\
C_2 &= (|15\rangle, |16\rangle, |25\rangle, |26\rangle)\\
C_3 &= (|13\rangle, |14\rangle, |23\rangle, |24\rangle)\,,
\end{aligned}$$

we have

$$\Gamma_\Psi = \begin{pmatrix} \boxed{G^3_\Psi} & & & \\ & \boxed{D^1_\Psi} & & \\ & & \boxed{D^2_\Psi} & \\ & & & \boxed{D^3_\Psi} \end{pmatrix}$$

where G^3_Ψ is defined in equation (3.3) and $D^i_\Psi = |x_i|^2 \cdot I_4$.

Rewriting G^n_Ψ as

$$G^n_\Psi = I_n - 2\begin{pmatrix} |x_1|^2 & & \\ & \ddots & \\ & & |x_n|^2 \end{pmatrix} + \begin{pmatrix} \overline{x_1} \\ \vdots \\ \overline{x_n} \end{pmatrix}(x_1, \ldots, x_n)$$

and applying the matrix determinant lemma

$$\det\left(A + uv^T\right) = \left(1 + v^T A^{-1} u\right)\det(A)$$

for all vectors u, v and invertible matrices A, we can explicitly derive the characteristic polynomial of G^n_Ψ, namely

$$\chi_T(G^n_\Psi) = \left(1 - \sum_{i=1}^{n} \frac{r_i}{T + 2\,r_i - 1}\right)\prod_{i=1}^{n}(T + 2\,r_i - 1)\,, \quad r_i := |x_i|^2\,.$$

In particular, the eigenvalues depend on $|x_i|^2$ only. For $K = 6$ and $K = 8$ this yields

$$\begin{aligned}
\chi_T(G^3_\Psi) &= T^3 - 2\,T^2 + T - 4\,r_1 r_2 r_3,\\
\chi_T(G^4_\Psi) &= T^4 - 3\,T^3 + 3\,T^2 - \left(1 + \sum_{i<j<k} r_i r_j r_k\right)T\\
&\quad - 16\,r_1 r_2 r_3 r_4 + 4\sum_{i<j<k} r_i r_j r_k.
\end{aligned}$$

In the following we explicitly calculate the eigenvalues of Γ_Ψ for arbitrary Ψ and $K = 6, N = 4$. From the above arguments, these are exactly

$$\{r_1, r_2, r_3\} \cup \left\{T \,:\, T^3 - 2\,T^2 + T - 4\,r_1 r_2 r_3 = 0\right\}$$

with $r_i \geq 0$ and $\sum_{i=1}^{3} r_i = 1$. In particular, $u := r_1 r_2 r_3$ covers the range $[0, \frac{1}{27}]$. Let λ_1 be the greatest root of $T^3 - 2\,T^2 + T - 4\,u$, then both remaining roots $\lambda_{2,3}$ can be expressed in terms of λ_1, yielding

$$\lambda_{2,3} = 1 - \frac{\lambda_1}{2} \pm \sqrt{\lambda_1 \left(1 - \frac{3}{4}\lambda_1\right)}. \tag{3.4}$$

Note that this term depends on u (that is, Ψ) only indirectly via λ_1! Figure 3.2 shows a plot of (3.4), from which we deduce that $\lambda_1 \in \left[1, \frac{4}{3}\right]$ since $\lambda_1 \in [0, 1]$ would contradict λ_1 being the greatest root. Plugging in $u = 0$ and $u = \frac{1}{27}$ and using the fact that λ_1 depends continuously on u shows that λ_1 actually covers $\left[1, \frac{4}{3}\right]$. We remark the consistency with a result by Yang Yang (1962), the eigenvalues of Γ_Ψ being less or equal to $\frac{1}{2}\frac{N}{K}(K - N + 2)$.

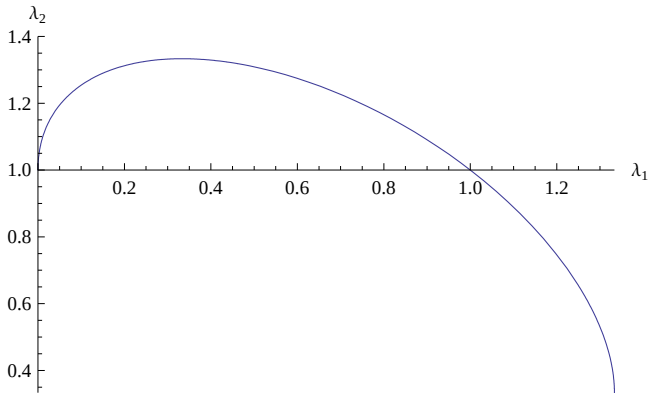

Figure 3.2: λ_2 vs. λ_1

3.6 Pair structure inheritance

Given a positive semidefinite operator[2] $h : \wedge^2\mathcal{H} \to \wedge^2\mathcal{H}$, we try to find the greatest eigenvalue of the corresponding N-body Hamiltonian H, additionally assuming that $K := \dim \mathcal{H}$ is even and h has a special form, namely

$$h = \sum_{i,j=1}^{K/2} h_{ij} |2i-1, 2i\rangle\langle 2j-1, 2j|$$

and a positive semidefinite matrix (h_{ij}). In N-body space,

$$H = \sum_{i,j=1}^{K/2} h_{ij}\, a^\dagger_{|2i-1,2i\rangle} a_{|2j-1,2j\rangle}.$$

[2]What follows applies literally to the minimization of $\langle \Psi \,|\, H\,\Psi \rangle$ for negative semidefinite h.

Define projectors

$$m_{1,i} := (1 - n_{2i-1})\, n_{2i},$$
$$m_{2,i} := n_{2i-1}\, (1 - n_{2i})$$

for all $i = 1, \ldots, K/2$, where $n_j = a_j^\dagger a_j$ is the number operator for state j. The intuitive picture behind $m_{2,i}$ is a number operator for "unlike pairs" as in figure 3.3. The decisive feature of these operators is the fact that they commute pairwise with themselves and with H, i.e.

$$[m_{p,i}, m_{q,j}] = 0 \quad \forall\, p, q \in \{1, 2\},\ i, j = 1, \ldots, K/2, \quad \text{and} \quad [H, m_{p,i}] = 0 \quad \forall\, p, i.$$

To proof the last equality, note that, for example,

$$m_{2,i}\, a^\dagger_{|2i-1,2i\rangle} = a^\dagger_{2i-1}\, a_{2i-1}\, a_{2i}\, a^\dagger_{2i} \cdot a^\dagger_{2i-1}\, a^\dagger_{2i} = 0.$$

The operator

$$m := \sum_{i=1}^{K/2} m_{1,i} + m_{2,i}$$

counts the total number of unlike pairs.

Figure 3.3: An "unlike pair"

The next proposition establishes that eigenvectors of H inherit the pair structure of h.

Proposition 18. *Each normalized eigenvector Ψ of H corresponding to the greatest eigenvalue can be chosen such that it has minimal number of unlike pairs, i.e., $\langle \Psi \,|\, m\, \Psi \rangle = 0$ if N is even and $\langle \Psi \,|\, m\, \Psi \rangle = 1$ if N is odd.*

Proof. We may assume that Ψ is also an eigenvector of $m_{p,i}\ \forall\, p, i$ and thus an eigenvector of m. Now suppose, on the contrary, that $\langle \Psi \,|\, m\, \Psi \rangle \geq 2$, then there are $i < j$ and $p, q \in \{1, 2\}$ with $m_{p,i}\, \Psi = \Psi$ and $m_{q,j}\, \Psi = \Psi$, w.l.o.g. $p = 1$, $q = 2$. We transform Ψ as shown in figure 3.4, or more formally:

$$\tilde{\Psi} := a^\dagger_{2i-1} a_{2j-1} \Psi.$$

$\tilde{\Psi}$ is a normalized eigenvector of $m_{p,k}\ \forall\, p, k$ which reduces the number of unlike pairs by two, and has the following property:

$$\left\langle \tilde{\Psi} \,|\, a^\dagger_{|2k-1,2k\rangle} a_{|2l-1,2l\rangle}\, \tilde{\Psi} \right\rangle = \begin{cases} \left\langle \Psi \,|\, a^\dagger_{|2k-1,2k\rangle} a_{|2l-1,2l\rangle}\, \Psi \right\rangle, & l \notin \{i, j\} \\ 0, & l = j \\ \delta_{kl} & l = i \end{cases}$$

for all k, l. As an immediate consequence,

$$\left\langle \tilde{\Psi} \,|\, H \tilde{\Psi} \right\rangle - \langle \Psi \,|\, H \Psi \rangle = h_{ii} \geq 0.$$

Since Ψ maximizes $\langle \Psi \,|\, H \Psi \rangle$, h_{ii} must be 0, and $\tilde{\Psi}$ is also an eigenvector of H corresponding to the greatest eigenvalue. This establishes the proposition. □

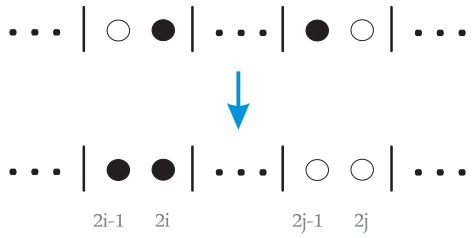

Figure 3.4: Collapse of two unlike pairs

With this proposition in mind, the next general idea is to work effectively with one-body instead of two-body reduced density matrices. To this end we project onto the pair structure as depicted in figure 3.5 for a single Slater determinant, or more formally,

$$P_{\text{pair}} = \prod_{i=1}^{K/2} \left[n_{2i-1} n_{2i} + (1 - n_{2i-1}) (1 - n_{2i}) \right]$$

with the well-known single-particle number operator $n_i = a_i^\dagger a_i$. Now introduce

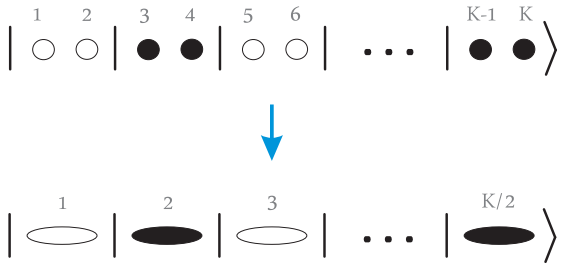

Figure 3.5: Effective pair structure

pair creation and annihilation operators,

$$b_i^\dagger := a_{|2i-1,2i\rangle}^\dagger = a_{2i-1}^\dagger a_{2i}^\dagger,$$
$$b_i := a_{|2i-1,2i\rangle} = a_{2i} a_{2i-1}$$

for all $i = 1, \ldots, K/2$, with the following *commutator relations* on the pair structure Hilbert space:

$$[b_i, b_j] = 0, \quad \left[b_i^\dagger, b_j^\dagger \right] = 0,$$
$$\left[b_i, b_j^\dagger \right] = \delta_{ij} \left(1 - 2 b_i^\dagger b_i \right) \quad \text{for all } i, j.$$

In particular, the "pair particles" acquire bosonic character as expected, but nevertheless $\left[b_i, b_i^\dagger \right] \neq 0$ in general.

Concluding, we have taken the first steps to reduce the problem $\arg\max_\Psi \langle \Psi \,|\, H \, \Psi \rangle$ on the $\binom{K}{N}$-dimensional Hilbert space $\wedge^N \mathcal{H}$ to a similar problem on the $\binom{K/2}{N/2}$-dimensional pair Hilbert space.

3.7 Numerics-based conjectures

Numerical experiments give rise to the following conjectures:

- For general p, γ^p_Ψ is an orthogonal projection if and only if Ψ is a Slater determinant, i.e., the generalization of proposition 7 holds.
- $\max_\Psi \|\gamma^p_\Psi\|_{\text{fro}}$ is reached if and only if γ^p_Ψ is an orthonormal projection (i.e. the maximum is $\binom{N}{p}$).

Chapter 4

The Periodic Table Revisited

In this chapter we introduce the FermiFab[1] Matlab toolbox which casts the perturbation-theory (PT) and full configuration interaction (FCI) models developed by Friesecke and Goddard (2008b,a) into an automated computation pipeline. Comparing the results for the atoms lithium – neon previously obtained "by hand" with the toolbox output verifies the correctness of the pipeline. Next, we use the toolbox to calculate the simultaneous angular momentum and spin eigenspaces of potassium – zinc, assuming that all orbitals up to $3p$ are permanently occupied, so the remaining degrees of freedom stem from the occupation of the $3d$ and $4s$ orbitals. These eigenspaces block-diagonalize the Hamiltonian and thus simplify the diagonalization task significantly.

4.1 Many-particle theory for atomic shell electrons

In this section we recall the main results by Friesecke and Goddard (2008b). N always denotes the number of electrons and $Z > 0$ the nuclear charge. Since we investigate also ions, not only neutral atoms, we don't fix $Z = N$.

The atoms are treated in the Born-Oppenheimer approximation, that is, the nucleus is assumed to be fixed, only the electron dynamics is investigated. The time-independent nonrelativistic Schrödinger equation reads $H\Psi = E\Psi$ with the Hamiltonian

$$H = H_0 + V_{ee}, \tag{4.1}$$

where in atomic units[2]

$$H_0 = \sum_{i=1}^{N} \left(-\frac{1}{2}\,\Delta_i - \frac{Z}{|\boldsymbol{x}_i|} \right), \quad V_{ee} = \sum_{i<j} \frac{1}{|\boldsymbol{x}_i - \boldsymbol{x}_j|}. \tag{4.2}$$

The $\boldsymbol{x}_i \in \mathbb{R}^3$ are the electronic coordinates. H_0 contains the kinetic energy and external potential arising from the nucleus, whereas V_{ee} describes the inter-electron Coulomb repulsion. The antisymmetric wavefunction $\Psi\left(\boldsymbol{x}_1, s_1, \ldots, \boldsymbol{x}_N, s_N\right)$ depends on both spatial and spin coordinates $s_i \in \{\uparrow, \downarrow\}$. For simplicity we work

[1] http://sourceforge.net/projects/fermifab

[2] For each $\boldsymbol{x} \in \mathbb{R}^3$, we set $|\boldsymbol{x}| := \|\boldsymbol{x}\|_2$.

in atomic units, that is, the electron mass m_e, the Planck constant $\hbar$ and the electron charge e are all set to 1.

The symmetry group of the Hamiltonian (4.1) is $SO(3) \times SU(2) \times \mathbb{Z}_2$ corresponding to total angular momentum, spin and parity, respectively. These operators are $\boldsymbol{L}^2 = L_x^2 + L_y^2 + L_z^2$ with $\boldsymbol{L} \equiv (L_x, L_y, L_z)$ given by

$$\boldsymbol{L} = \sum_{i=1}^{N} \boldsymbol{L}_i,$$

where $\boldsymbol{L}_i$ is the single-body angular momentum operator acting on particle i. The same relations hold for $\boldsymbol{S}$. The N-body parity operator R is defined by

$$R\,\Psi\left(\boldsymbol{x}_1, s_1, \ldots, \boldsymbol{x}_N, s_N\right) = \Psi\left(-\boldsymbol{x}_1, s_1, \ldots, -\boldsymbol{x}_N, s_N\right).$$

We recall the following well known facts.

Lemma 19.

1. *For arbitrary N and Z, a set of operators which commutes with the Hamiltonian H and with each other is given by*

$$\boldsymbol{L}^2,\ L_3,\ \boldsymbol{S}^2,\ S_3,\ R. \tag{4.3}$$

2. *The eigenvalues of $\boldsymbol{L}^2$, $\boldsymbol{S}^2$, and R – acting on $L_a^2\left((\mathbb{R}_3 \times \mathbb{Z}_2)^N\right)$ – are, respectively,*

$$L(L+1), \quad L = 0, 1, 2, \ldots \tag{4.4}$$

$$S(S+1), \quad S = \begin{cases} \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots, \frac{N}{2}, & N \text{ odd}, \\ 0, 1, 2, \ldots, \frac{N}{2}, & N \text{ even} \end{cases} \tag{4.5}$$

$$p, \quad p = \pm 1. \tag{4.6}$$

3. *For fixed L, S and p, on any joint eigenspace of H, $\boldsymbol{L}^2$, $\boldsymbol{S}^2$ and R, L_3 has eigenvalues $M = -L, -L+1, \ldots, L$, and S_3 has eigenvalues $M_S = -S, -S+1, \ldots, S$. In particular, the eigenspace has dimension greater or equal to $(2L+1) \cdot (2S+1)$, with equality in the case when the joint eigenspaces of H and the operators* (4.3) *are non-degenerate (i.e., one-dimensional).*

Note that using the operators $L_\pm = L_x \pm iL_y$ and $S_\pm = S_x \pm iS_y$, one can traverse all eigenspaces of L_3 and S_3, respectively.

The basic idea behind the perturbation theory (PT) model consists of rescaling the Schrödinger equation and defining a Z-independent Hamiltonian

$$\tilde{H}_0 = \sum_{i=1}^{N} \left(-\frac{1}{2}\Delta_i - \frac{1}{|\boldsymbol{x}_i|} \right), \quad \tilde{E} = \frac{1}{Z^2}\, E. \tag{4.7}$$

Now we can finally state the PT model, which is derived and rigorously justified by Friesecke and Goddard (2008b).

$$\begin{aligned} &PHP\Psi = E\Psi, \quad \Psi \in V_0, \quad P = \text{ orthogonal projector onto } V_0, \\ &\qquad V_0 = \text{ ground state eigenspace of } H_0 \end{aligned} \tag{4.8}$$

Theorem 20. *Let $N = 1, \dots, 10$ and $Z > 0$, and let $n(N)$ be the number of energy levels of the PT model* (4.8)*. Then:*

1. *For all sufficiently large Z, the lowest $n(N)$ energy levels $E_1(N,Z) < \cdots < E_{n(N)}(N,Z)$ of the full Hamiltonian* (4.1) *have exactly the same dimension, total spin quantum number, total angular momentum quantum number, and parity as the corresponding PT energy levels $E_1^{\mathrm{PT}}(N,Z) < \cdots < E_{n(N)}^{\mathrm{PT}}(N,Z)$.*

2. *The lowest $n(N)$ energy levels of the full Hamiltonian have the asymptotic expansion*

$$\begin{aligned} \frac{E_j(N,Z)}{Z^2} &= \frac{E_j^{\mathrm{PT}}(N,Z)}{Z^2} + O\left(\frac{1}{Z^2}\right) \\ &= \tilde{E}^{(0)} + \frac{1}{Z}\,\tilde{E}_j^{(1)} + O\left(\frac{1}{Z^2}\right) \text{ as } Z \to \infty, \end{aligned} \tag{4.9}$$

   where $\tilde{E}^{(0)}$ is the lowest eigenvalue of $\tilde{H}_0$ and the $\tilde{E}_j^{(1)}$ are the energy levels of $\tilde{P}V_{ee}\tilde{P}$ on $\tilde{V}_0$.

3. *The projectors $P_1, \dots, P_{n(N)}$ onto the lowest $n(N)$ eigenspaces of the full Hamiltonian satisfy*[3]

$$\left\| P_j - P_j^{\mathrm{PT}} \right\| = O\left(\frac{1}{Z}\right) \text{ as } Z \to \infty, \tag{4.10}$$

   where the P_j^{PT} are the corresponding projectors for the PT model.

4.2 Orbital occupation in transition metals

To extend the ideas by Friesecke and Goddard (2008a) to the atoms potassium – zinc, we first choose an explicit representation of the single-particle dilated hydrogen orbitals up to $4s$ in equation (4.11) below. The "original" orbitals can be regained by plugging the nuclear charge Z into the dilation parameters Z_i for all $i = 1, \dots, 7$. For brevity's sake we have omitted the spin here, which is

[3] Here, $\|\cdot\|$ is the usual operator norm.

just a multiplication by $|\uparrow\rangle$ or $|\downarrow\rangle$, and we have set $r \equiv |\boldsymbol{x}|$.

$$
\begin{aligned}
\varphi_{1s}(\boldsymbol{x}) &= \frac{Z_1^{\frac{3}{2}}}{\sqrt{\pi}} \mathrm{e}^{-Z_1 r} \\
\varphi_{2s}(\boldsymbol{x}) &\sim \left(1 - \frac{1}{2}\frac{2Z_1 + Z_2}{3} r\right) \mathrm{e}^{-Z_2 r/2} \\
\varphi_{2\mathrm{pi}}(\boldsymbol{x}) &= \frac{Z_3^{5/2}}{\sqrt{32\pi}}\, x_i\, \mathrm{e}^{-Z_3 r/2}, \quad i = 1,2,3 \\
\varphi_{3s}(\boldsymbol{x}) &\sim \left(1 - \frac{2}{3} c_1 r + \frac{2}{27} c_2 r^2\right) \mathrm{e}^{-Z_4 r/3} \\
\varphi_{3\mathrm{pi}}(\boldsymbol{x}) &= \frac{2}{27}\left(\frac{10 Z_5^7}{\pi\left(9Z_3^2 - 8Z_3 Z_5 + 4Z_5^2\right)}\right)^{1/2} x_i \left(1 - \frac{1}{6}\frac{3Z_3 + 2Z_5}{5} r\right) \mathrm{e}^{-Z_5 r/3} \\
\varphi_{3\mathrm{d0}}(\boldsymbol{x}) &= \frac{1}{81}\sqrt{\frac{Z_6^3}{6\pi}}\left(3x_3^2 - r^2\right) Z_6^2 \mathrm{e}^{-Z_6 r/3} \\
\varphi_{3\mathrm{dz}}(\boldsymbol{x}) &= \frac{2}{81}\sqrt{\frac{Z_6^3}{2\pi}}\, x_1 x_2 Z_6^2 \mathrm{e}^{-Z_6 r/3} \\
\varphi_{3\mathrm{dm}}(\boldsymbol{x}) &= \frac{1}{81}\sqrt{\frac{Z_6^3}{2\pi}}\left(x_1^2 - x_2^2\right) Z_6^2 \mathrm{e}^{-Z_6 r/3} \\
\varphi_{3\mathrm{dx}}(\boldsymbol{x}) &= \frac{2}{81}\sqrt{\frac{Z_6^3}{2\pi}}\, x_2 x_3 Z_6^2 \mathrm{e}^{-Z_6 r/3} \\
\varphi_{3\mathrm{dy}}(\boldsymbol{x}) &= \frac{2}{81}\sqrt{\frac{Z_6^3}{2\pi}}\, x_1 x_3 Z_6^2 \mathrm{e}^{-Z_6 r/3} \\
\varphi_{4s}(\boldsymbol{x}) &\sim \left(1 - \frac{3}{4} e_1 r + \frac{1}{8} e_2 r^2 - \frac{1}{192} e_3 r^3\right) \mathrm{e}^{-Z_7 r/4}
\end{aligned}
\tag{4.11}
$$

The real constants c_1, c_2 and e_1, e_2, e_3 are determined by the L^2 orthonormalization constraints of the orbitals. For the original orbitals ($Z_i \to Z$), these constants are

$$c_1 \to Z,\ c_2 \to Z^2,\ e_1 \to Z,\ e_2 \to Z^2,\ e_3 \to Z^3.$$

Note that all orbitals are chosen real to simplify computations.

A matrix representation of the $\boldsymbol{L}$ operator acting on the d-orbitals can be calculated, e.g., by a computer algebra system[4]; let P_d be the projector on $(\varphi_{3\mathrm{d0}}, \varphi_{3\mathrm{dz}}, \varphi_{3\mathrm{dm}}, \varphi_{3\mathrm{dx}}, \varphi_{3\mathrm{dy}})$, then one obtains

$$P_d \boldsymbol{L} P_d = \left(\begin{pmatrix} 0 & & & \sqrt{3}\,i & \\ & 0 & & i & -i \\ & & 0 & i & \\ -\sqrt{3}\,i & -i & -i & 0 & \\ & i & & & 0 \end{pmatrix}, \begin{pmatrix} 0 & & & & -\sqrt{3}\,i \\ & 0 & & i & \\ & & 0 & i & \\ & -i & -i & 0 & \\ \sqrt{3}\,i & & & & 0 \end{pmatrix}, \begin{pmatrix} 0 & & & & \\ & 0 & 2\,i & & \\ & -2\,i & 0 & & \\ & & & 0 & i \\ & & & -i & 0 \end{pmatrix}\right).$$

The Matlab file periodic_table/calc_simLS.m of the FermiFab toolbox calculates the simultaneous $\boldsymbol{L}^2, L_3, \boldsymbol{S}^2, S_3, R$ eigenspaces of the input atom, w.l.o.g. choosing $L_3 \equiv 0$ and S_3 maximal. It uses the method fermifab/simdiag.m which implements the simultaneous diagonalization of commuting normal matrices (Bunse-Gerstnert et al. 1993; Goldstine and Horwitz 1959). In our case,

[4] See periodic_table/symbolic_base/angularY2.nb.

the parity quantum number yields no additional information since the $3d$ and $4s$ orbitals are both of even parity. The results for the atoms potassium, calcium, copper and zinc are shown in table 4.2. For brevity's sake we haven't printed all transition metals.[5]

	sym.	$\boldsymbol{L}^2$	$\boldsymbol{S}^2$	S_3	config.	Ψ
K	^2S	0	$\frac{3}{4}$	$\frac{1}{2}$	$[\mathrm{Ar}]\,4s^1$	$\lvert s\rangle$
	^2D	6	$\frac{3}{4}$	$\frac{1}{2}$	$[\mathrm{Ar}]\,3d^1$	$\lvert d_0\rangle$
Ca	^1S	0	0	0	$[\mathrm{Ar}]\,4s^2$	$\lvert s\overline{s}\rangle$
					$[\mathrm{Ar}]\,3d^2$	$\frac{1}{\sqrt{5}}\left(\lvert d_0\overline{d_0}\rangle + \lvert d_z\overline{d_z}\rangle + \lvert d_m\overline{d_m}\rangle + \lvert d_x\overline{d_x}\rangle + \lvert d_y\overline{d_y}\rangle\right)$
	^3P	2	2	1	$[\mathrm{Ar}]\,3d^2$	$\frac{1}{\sqrt{5}}\left(2\cdot\lvert d_z d_m\rangle + \lvert d_x d_y\rangle\right)$
	^1D	6	0	0	$[\mathrm{Ar}]\,3d^1\,4s^1$	$\frac{1}{\sqrt{2}}\left(\lvert d_0\overline{s}\rangle - \lvert\overline{d_0}s\rangle\right)$
					$[\mathrm{Ar}]\,3d^2$	$\frac{1}{\sqrt{14}}\left(-2\cdot\lvert d_0\overline{d_0}\rangle + 2\cdot\lvert d_z\overline{d_z}\rangle + 2\cdot\lvert d_m\overline{d_m}\rangle - \lvert d_x\overline{d_x}\rangle - \lvert d_y\overline{d_y}\rangle\right)$
	^3D	6	2	1	$[\mathrm{Ar}]\,3d^1\,4s^1$	$\lvert d_0 s\rangle$
	^3F	12	2	1	$[\mathrm{Ar}]\,3d^2$	$\frac{1}{\sqrt{5}}\left(-\lvert d_z d_m\rangle + 2\cdot\lvert d_x d_y\rangle\right)$
	^1G	20	0	0	$[\mathrm{Ar}]\,3d^2$	$\frac{1}{\sqrt{70}}\left(6\cdot\lvert d_0\overline{d_0}\rangle + \lvert d_z\overline{d_z}\rangle + \lvert d_m\overline{d_m}\rangle - 4\cdot\lvert d_x\overline{d_x}\rangle - 4\cdot\lvert d_y\overline{d_y}\rangle\right)$
Cu	^2S	0	$\frac{3}{4}$	$\frac{1}{2}$	$[\mathrm{Ar}]\,3d^{10}\,4s^1$	$\lvert d_0\overline{d_0}d_z\overline{d_z}d_m\overline{d_m}d_x\overline{d_x}d_y\overline{d_y}s\rangle$
	^2D	6	$\frac{3}{4}$	$\frac{1}{2}$	$[\mathrm{Ar}]\,3d^9\,4s^2$	$\lvert d_0 d_z\overline{d_z}d_m\overline{d_m}d_x\overline{d_x}d_y\overline{d_y}s\overline{s}\rangle$
Zn	^1S	0	0	0	$[\mathrm{Ar}]\,3d^{10}\,4s^2$	$\lvert d_0\overline{d_0}d_z\overline{d_z}d_m\overline{d_m}d_x\overline{d_x}d_y\overline{d_y}s\overline{s}\rangle$

Table 4.1: Simultaneous $\boldsymbol{L}^2, L_3, \boldsymbol{S}^2, S_3, R$ eigenspaces of K, Ca, Cu and Zn for $L_3 \equiv 0$ and maximal S_3.

What remains is the evaluation of the Coulomb integrals

$$(ab\,|\,cd) := \int_{\mathbb{R}^6} \overline{a(\boldsymbol{x}_1)}b(\boldsymbol{x}_1)\,\frac{1}{|\boldsymbol{x}_1-\boldsymbol{x}_2|}\,\overline{c(\boldsymbol{x}_2)}d(\boldsymbol{x}_2)\,\mathrm{d}\boldsymbol{x}_1\boldsymbol{x}_2 \tag{4.12}$$

for the spatial orbitals (4.11). Concerning the spin of the wavefunctions, consider

$$\psi_i(\boldsymbol{x},s) = \varphi_i(\boldsymbol{x})\alpha_i(s), \quad \boldsymbol{x}\in\mathbb{R}^3, s\in\{\uparrow,\downarrow\}$$

for $i=1,\ldots,4$. Then with $|\psi_i\psi_j\rangle = \frac{1}{\sqrt{2}}\left(\psi_i\otimes\psi_j - \psi_j\otimes\psi_i\right)$, we get

$$\begin{aligned}&\left\langle \psi_1\psi_2\,|\,\frac{1}{|\boldsymbol{x}_1-\boldsymbol{x}_2|}\psi_3\psi_4\right\rangle\\ &= (\varphi_1\varphi_3\,|\,\varphi_2\varphi_4)\,\langle\alpha_1\,|\,\alpha_3\rangle\,\langle\alpha_2\,|\,\alpha_4\rangle\\ &- (\varphi_1\varphi_4\,|\,\varphi_2\varphi_3)\,\langle\alpha_1\,|\,\alpha_4\rangle\,\langle\alpha_2\,|\,\alpha_3\rangle\,.\end{aligned} \tag{4.13}$$

[5]These can be found in the periodic_table/tables subfolder of the FermiFab toolbox.

We implement the ideas by Friesecke and Goddard (2008b) summarized in the following lemma. For the Fourier transformation $\mathcal{F}$ of a function $f \in L^1(\mathbb{R}^n)$, use the convention

$$(\mathcal{F}f)(k) := \int_{\mathbb{R}^n} f(x) \mathrm{e}^{-ik\cdot x} \, \mathrm{d}x.$$

Lemma 21. *For one-electron orbitals (φ_i) with φ_i and $\mathcal{F}\varphi_i \in L^2(\mathbb{R}^3) \cap L^\infty(\mathbb{R}^3)$, let $f(x) := \varphi_i(x)\overline{\varphi_j(x)}$ and $g(x) := \overline{\varphi_k(x)}\varphi_l(x)$. Then*

$$(\varphi_i\varphi_j \,|\, \varphi_k\varphi_l) = \frac{1}{2\pi^2} \int_{\mathbb{R}^3} \frac{1}{|\boldsymbol{k}|^2} \overline{(\mathcal{F}f)(\boldsymbol{k})} \, (\mathcal{F}g)(\boldsymbol{k}) \, \mathrm{d}^3\boldsymbol{k}.$$

In what follow, we explain the details of the symbolic "computation pipeline". For each $\boldsymbol{q} \in \mathbb{N}_0^3$, concisely write

$$\frac{\partial^{\boldsymbol{q}}}{\partial \boldsymbol{k}^{\boldsymbol{q}}} := \prod_{i=1}^{3} \frac{\partial^{q_i}}{\partial k_i^{q_i}}.$$

Let $f(x) = \varphi_i(x)\overline{\varphi_j(x)}$ as in lemma 21 with φ_i, φ_j from the set (4.11), then f can be expanded as

$$f(\boldsymbol{x}) = \sum_{n=0}^{6} r^n \left(\sum_{q_1,q_2,q_3=0}^{4} c_{n,\boldsymbol{q}} \cdot \prod_{i=1}^{3} x_i^{q_i} \right) \mathrm{e}^{-\lambda r}, \quad r = |\boldsymbol{x}|$$

with constants $c_{n,\boldsymbol{q}}$ and $\lambda > 0$. This is implemented by symbolic_base/coulomb.nb. Directly from the definition of the Fourier transform, it follows that

$$(\mathcal{F}f)(\boldsymbol{k}) = \sum_{n,\boldsymbol{q}} c_{n,\boldsymbol{q}} \, (-1)^n \frac{\partial^n}{\partial \lambda^n} \, i^{q_1+q_2+q_3} \frac{\partial^{\boldsymbol{q}}}{\partial \boldsymbol{k}^{\boldsymbol{q}}} \left(\mathcal{F}\mathrm{e}^{-\lambda r}\right)(\boldsymbol{k}). \tag{4.14}$$

One calculates

$$\left(\mathcal{F}\mathrm{e}^{-\lambda r}\right)(\boldsymbol{k}) = \frac{8\lambda\pi}{\left(\lambda^2 + k^2\right)^2},$$

so precomputing[6] the following integral over polar coordinates

$$I_{\boldsymbol{q},\boldsymbol{q}'}(\lambda,\lambda') := (-i)^{q_1+q_2+q_3} \, i^{q_1'+q_2'+q_3'} \frac{1}{2\pi^2} \times \int_0^\infty \int_0^\pi \int_0^{2\pi} \left(\frac{\partial^{\boldsymbol{q}}}{\partial \boldsymbol{k}^{\boldsymbol{q}}} \frac{8\lambda\pi}{\left(\lambda^2+k^2\right)^2} \right) \left(\frac{\partial^{\boldsymbol{q}'}}{\partial \boldsymbol{k}^{\boldsymbol{q}'}} \frac{8\lambda'\pi}{\left(\lambda'^2+k^2\right)^2} \right) \sin\vartheta \, \mathrm{d}\varphi \, \mathrm{d}\vartheta \, \mathrm{d}k$$

with $k \equiv |\boldsymbol{k}|$ yields for the spatial orbitals

$$\hat{v}_{ee,ijkl} := (\varphi_i\varphi_j \,|\, \varphi_k\varphi_l) = \sum_{n,n'} \sum_{\boldsymbol{q},\boldsymbol{q}'} \overline{c_{n,\boldsymbol{q}}} \, c_{n',\boldsymbol{q}'} \cdot (-1)^{n+n'} \frac{\partial^n}{\partial\lambda^n} \frac{\partial^{n'}}{\partial\lambda'^{n'}} I_{\boldsymbol{q},\boldsymbol{q}'}(\lambda,\lambda').$$

[6] See the Mathematica file symbolic_base/precompute.nb.

This (time consuming) computation is performed in symbolic_base/coulomb.nb, which also handles the coefficients $c_{n,\boldsymbol{q}}$. Considering symmetry, it follows directly from definition (4.12) that $(ab\,|\,cd) = (cd\,|\,ab)$. Furthermore, plugging in the orbitals (4.11) and realizing that they are chosen real, we may also exchange $a \leftrightarrow b$ and $c \leftrightarrow d$, i.e. we need only compute $\hat{v}_{ee,ijkl}$ for $(i,j) \leq (k,l)$ in lexicographical order.

Let V_{ee} be the N-particle Coulomb operator obtained from the two-particle operator v_{ee}, and χ, ψ wavefunctions in N-particle space, including spin. Indexing spatial orbitals (4.11) by i,j,k,l and the spin-part by $\alpha,\beta,\gamma,\delta$, we get a spatial RDM mapping as follows.[7]

$$\begin{aligned}
\langle \chi \,|\, V_{ee}\psi\rangle &= \operatorname{tr}\left[V_{ee}|\psi\rangle\langle\chi|\right] = \operatorname{tr}_{\wedge^2\mathcal{H}}\left[v_{ee}\Gamma_{|\psi\rangle\langle\chi|}\right] \\
&= \sum_{\substack{i\alpha<k\beta \\ j\gamma<l\delta}} \langle i\alpha, k\beta \,|\, v_{ee} \,|\, j\gamma, l\delta\rangle \left\langle j\gamma, l\delta \,|\, \Gamma_{|\psi\rangle\langle\chi|} \,|\, i\alpha, k\beta\right\rangle \overset{(4.13)}{=} \\
&= \sum_{\substack{i\alpha<k\beta \\ j\gamma<l\delta}} (ij\,|\,kl) \left\langle j\alpha, l\beta \,|\, \Gamma_{|\psi\rangle\langle\chi|} \,|\, i\alpha, k\beta\right\rangle \\
&\quad - \sum_{\substack{i\alpha<k\beta \\ l\beta<j\alpha}} (ij\,|\,kl) \left\langle l\beta, j\alpha \,|\, \Gamma_{|\psi\rangle\langle\chi|} \,|\, i\alpha, k\beta\right\rangle \\
&= \sum_{ij,kl} (ij\,|\,kl) \sum_{\substack{\alpha,\beta \\ i\alpha<k\beta}} \left\langle j\alpha, l\beta \,|\, \Gamma_{|\psi\rangle\langle\chi|} \,|\, i\alpha, k\beta\right\rangle \\
&= \operatorname{tr}\left[\hat{v}_{ee}\,\hat{\Gamma}_{|\psi\rangle\langle\chi|}\right]
\end{aligned} \tag{4.15}$$

with

$$\left(\hat{\Gamma}_{|\psi\rangle\langle\varphi|}\right)_{kl,ij} := \sum_{\substack{\alpha,\beta \\ i\alpha<k\beta}} \left\langle j\alpha, l\beta \,|\, \Gamma_{|\psi\rangle\langle\varphi|} \,|\, i\alpha, k\beta\right\rangle .$$

A similar equation can be obtained for single-particle operators. The crucial feature is that $\hat{\Gamma}_{|\psi\rangle\langle\varphi|}$ is just an algebraic coefficient mapping and doesn't depend on the choice of the dilation parameters Z_i, in particular if ψ and χ belong to a degenerate $\boldsymbol{L}^2, L_3, \boldsymbol{S}^2, S_3, R$-eigenspace. So $\hat{\Gamma}_{|\psi\rangle\langle\varphi|}$ can be precomputed without any reference to the Hamiltonian at all. Instead, the dilation parameters come in via the Couloumb integrals in $\hat{v}_{ee}$. So equation (4.15) speeds up the energy minimization in periodic_table/levels_dil.m immensely since the most time consuming part is plugging in the Z_i.

Finally, the results for both "original" and "dilated" Hydrogen orbitals are shown in figure 4.1. It follows from the min-max principle that the theoretical model provides an upper bound on the actual ground state energy, which is in perfect agreement with the obtained data. Table 4.2 contains the quantitative deviation and shows that numerical optimization of the dilation parameters Z_i reduces the error to approximately a tenth.

Tables 4.2 and 4.2 confirm the predictive power of the FCI model. To obtain the correct values for chromium and copper, too, one could include the $3s$ and $3p$ orbitals or even contributions from higher shells.

[7] Refer to mex/gen_rdm_coulomb.cpp for an implementation.

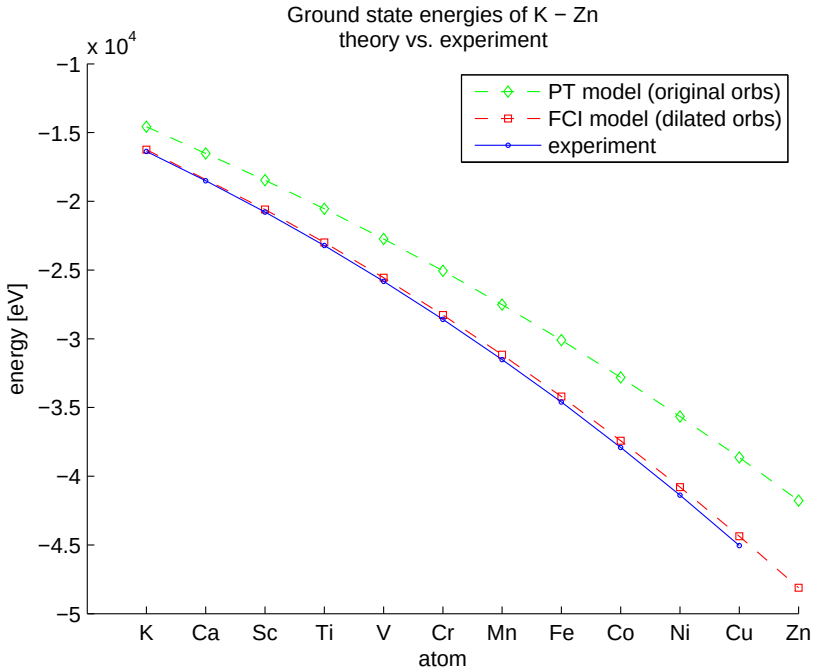

Figure 4.1: Ground state energy of K – Zn using original and dilated $3d, 4s$ hydrogen orbitals ($3s$ and $3p$ are assumed to be permanently filled). The theoretical FCI-model value for calcium is missing since the numeric minimization routine reported "division by zero". The experimental ionization energies are taken from Lide (2003).

atom	K	Ca	Sc	Ti	V	Cr
PT (original orbs)	11.1%	10.7%	11.1%	11.5%	11.9%	12.3%
FCI (dilated orbs)	0.9%	n.a.	0.9%	1.0%	1.0%	1.1%
atom	Mn	Fe	Co	Ni	Cu	Zn
PT (original orbs)	12.7%	13.0%	13.5%	13.8%	14.2%	n.a.
FCI (dilated orbs)	1.1%	1.2%	1.3%	1.4%	1.5%	n.a.

Table 4.2: Relative ground state error of the PT and FCI models

atom	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
theory	^2S	n.a.	^2D	^3F	^4F	^5D	^6S	^5D	^4F	^3F	^2D	^1S
experiment	^2S	^1S	^2D	^3F	^4F	^7S	^6S	^5D	^4F	^3F	^2S	^1S

Table 4.3: Ground state symmetry quantum numbers, FCI model (dilated orbitals)

atom	K	Ca	Sc	Ti	V	Cr
theory $[Ar]$	$4s$	n.a.	$3d\,4s^2$	$3d^2\,4s^2$	$3d^3\,4s^2$	$3d^4\,4s^2$
experiment $[Ar]$	$4s$	$4s^2$	$3d\,4s^2$	$3d^2\,4s^2$	$3d^3\,4s^2$	$3d^5\,4s$
atom	Mn	Fe	Co	Ni	Cu	Zn
theory $[Ar]$	$3d^5\,4s^2$	$3d^6\,4s^2$	$3d^7\,4s^2$	$3d^8\,4s^2$	$3d^9\,4s^2$	$3d^{10}\,4s^2$
experiment $[Ar]$	$3d^5\,4s^2$	$3d^6\,4s^2$	$3d^7\,4s^2$	$3d^8\,4s^2$	$3d^{10}\,4s$	$3d^{10}\,4s^2$

Table 4.4: Ground state configuration as predicted by the FCI model (dilated orbitals)

Chapter 5

Conclusion

The central new results in chapter 3 are the detailed spectral analysis of Γ_Ψ in section 3.5 for small dimensions, and the pair structure inheritance in section 3.6. There we have shown that a special pair structure of the two-body interaction Hamiltonian h translates to the eigenfunctions of the N-body Hamiltonian and thus reduces the system complexity significantly. Due to the Coleman expansion theorem, this structure can always be assumed if, e.g., h has rank 1 . We hope that eventually an effective "single-pair-particle" Hamiltonian can be derived – similar to Cooper pairs of electrons.

In chapter 4 we have extended the calculations by Friesecke and Goddard (2008b,a) to transition metals. Due to the increasing complexity, we have developed an automated "symbolic computation pipeline" comprising Mathematica, Matlab and – via the symbolic toolbox – Maple. Thus we have been able to verify the calculations of Friesecke and Goddard (2008b) and compare the predictions of the FCI model for transition metals with experimental data in section 4.2. We observe inter alia that the ground state $3d$ vs. $4s$ occupation is captured correctly for all investigated elements, except for copper and chromium.

Since we have mainly focused on the FCI model, what remains open to further research is the application of the PT model to the rest of the periodic table. As long as the nuclear charge is fairly small, i.e., relativistic effects are still negligible, theorem 20 (Friesecke and Goddard 2008b) provides a calculation scheme for the angular momentum and spin quantum numbers of the ground state for sufficiently large Z. Thus we hope that eventually, a deeper understanding of the periodic table based on ab inito principles can be attained.

Appendix A

Basic Properties of Integral Operators

Theorem 22. *Let $(\Omega, \mathcal{A}, \mu)$ be a σ-finite measure space and $\gamma \in L^2(\Omega \times \Omega, \mathbb{C})$ such that $\gamma(x,y) = \overline{\gamma(y,x)}$ $\forall x, y \in \Omega$. Then*

$$\Gamma : \ L^2(\Omega, \mathbb{C}) \to L^2(\Omega, \mathbb{C}), \ (\Gamma\varphi)(x) := \int \gamma(x,y)\varphi(y)\,\mathrm{d}y$$

is linear, compact and self-adjoint.

Proof. Γ is well-defined: by a theorem of measure and integration theory,

$$\gamma_x : \ y \mapsto \overline{\gamma(x,y)} \ \in L^2(\Omega, \mathbb{C})$$

for almost all $x \in \Omega$. Using the inner product of $L^2(\Omega, \mathbb{C})$, we may write

$$(\Gamma\varphi)(x) = \langle \gamma_x \,|\, \varphi \rangle .$$

Thus

$$\int |(\Gamma\varphi)(x)|^2 \,\mathrm{d}x \le \int \|\gamma_x\|^2 \, \|\varphi\|^2 \,\mathrm{d}x = \left(\int\int |\gamma(x,y)|^2 \,\mathrm{d}y \,\mathrm{d}x \right) \|\varphi\|^2 < \infty.$$

Γ is compact: let $(\varphi_i)_{i\in\mathbb{N}}$ be a bounded sequence in $L^2(\Omega, \mathbb{C})$. Then there exists a weakly convergent subsequence (also denoted by (φ_i)), i.e. $\varphi_i \rightharpoonup \varphi \in L^2(\Omega, \mathbb{C})$. Therefore

$$(\Gamma\varphi_i)(x) = \langle \gamma_x \,|\, \varphi_i \rangle \to \langle \gamma_x \,|\, \varphi \rangle = (\Gamma\varphi)(x) \quad \text{for almost all } x \in \Omega.$$

Choose $M \in \mathbb{R}$ such that $\|\varphi_i\| \le M$ for all $i \in \mathbb{N}$, then

$$|(\Gamma\varphi_i)(x)| = |\langle \gamma_x \,|\, \varphi_i \rangle| \le M \cdot \|\gamma_x\| \in L^2(\Omega, \mathbb{C}).$$

The theorem of dominated convergence now yields $\Gamma\varphi_i \xrightarrow{L^2} \Gamma\varphi$.

Γ is self-adjoint: for all $\varphi, \psi \in L^2(\Omega, \mathbb{C})$ we have

$$\langle \psi \,|\, \Gamma\varphi \rangle = \int\int \overline{\psi(x)}\gamma(x,y)\varphi(y)\,\mathrm{d}y\,\mathrm{d}x = \int\int \overline{\gamma(y,x)\psi(x)}\varphi(y)\,\mathrm{d}x\,\mathrm{d}y = \langle \Gamma\psi \,|\, \varphi \rangle .$$

□

Now, let further $L^2(\Omega, \mathbb{C})$ be separable, e.g. $(\Omega, \mathcal{A}, \mu) = (\mathbb{R}^N, \mathcal{B}, \lambda)$.

Proposition 23. *Let Γ be positive semidefinite. Then*

$$\operatorname{tr} \Gamma = \int \gamma(x, x) \, \mathrm{d}x \in [0, \infty].$$

Proof. By the spectral theorem for compact, self-adjoint operators, Γ has a complete orthonormal system $(\psi_i)_{i \in \mathbb{N}}$ of eigenvectors with corresponding eigenvalues $\lambda_i \in \mathbb{R}$. That is,

$$\Gamma\varphi = \sum_i \lambda_i \langle \psi_i \,|\, \varphi \rangle \, \psi_i \quad \forall \varphi \in L^2(\Omega, \mathbb{C}), \quad \text{and}$$

$$\gamma_x = \sum_i \langle \psi_i \,|\, \gamma_x \rangle \, \psi_i = \sum_i \overline{(\Gamma\psi_i)(x)} \, \psi_i = \sum_i \lambda_i \, \overline{\psi_i(x)} \, \psi_i, \quad \text{i.e.}$$

$$\gamma(x, y) = \overline{\gamma_x(y)} = \sum_i \lambda_i \, \psi_i(x) \, \overline{\psi_i(y)}.$$

As Γ is positive semidefinite, $\lambda_i \geq 0 \ \forall i \in \mathbb{N}$; thus the theorem of monotone convergence yields

$$\operatorname{tr} \Gamma = \sum_i \lambda_i = \int \sum_i \lambda_i \, |\psi_i(x)|^2 \, \mathrm{d}x = \int \gamma(x, x) \, \mathrm{d}x.$$

□

Appendix B

The Tensor Product of Hilbert Spaces

Let $\mathcal{H}_1$ and $\mathcal{H}_2$ be Hilbert spaces over $\mathbb{K} = \mathbb{R}$ or $\mathbb{C}$ and $u \in \mathcal{H}_1$, $v \in \mathcal{H}_2$. Define

$$(u \otimes v)(w, z) := \langle w \,|\, u \rangle \langle z \,|\, v \rangle \quad \text{for all } w \in \mathcal{H}_1,\ z \in \mathcal{H}_2.$$

$u \otimes v$ is a conjugate bilinear form on $\mathcal{H}_1 \times \mathcal{H}_2$. Note that $u \otimes v$ equals $u' \otimes v'$ if and only if the corresponding forms are identical and that $\otimes$ behaves like a product, i.e.

$$(\alpha u + u') \otimes v = \alpha (u \otimes v) + (u' \otimes v), \quad \alpha \in \mathbb{K}$$

and similarly for $u \otimes (\alpha v + v')$. Denote the set of all finite linear combinations of such forms by $(\mathcal{H}_1 \otimes \mathcal{H}_2)_{\text{pre}}$. This becomes a pre-Hilbert space with the inner product

$$\langle u \otimes v \,|\, w \otimes z \rangle := \langle u \,|\, w \rangle \langle v \,|\, z \rangle = (w \otimes z)(u, v),$$

extending linearly. To show that this definition doesn't depend on the choice of representatives, first let μ be a finite linear combination which is the zero form. Then

$$\langle u \otimes v \,|\, \mu \rangle = \mu(u, v) = 0 \quad \text{for all } u \in \mathcal{H}_1,\ v \in \mathcal{H}_2$$

and by linearity $\langle \lambda \,|\, \mu \rangle = 0$ for all $\lambda \in (\mathcal{H}_1 \otimes \mathcal{H}_2)_{\text{pre}}$. Given finite sums $\lambda, \lambda', \mu, \mu'$ with $\lambda = \lambda'$ and $\mu = \mu'$, we now have

$$\langle \lambda \,|\, \mu \rangle - \langle \lambda' \,|\, \mu' \rangle = \langle \lambda \,|\, \mu - \mu' \rangle + \overline{\langle \mu' \,|\, \lambda - \lambda' \rangle} = 0.$$

Finally, we show that the inner product is positive definite. Suppose

$$\lambda = \sum_{i=1}^{N} \alpha_i (u_i \otimes v_i), \quad u_i \in \mathcal{H}_1,\ v_i \in \mathcal{H}_2.$$

Let $(w_i)_i$ and $(z_i)_i$ be finite orthonormal bases of $\operatorname{span}\{u_i\}_{i=1\ldots N}$ and $\operatorname{span}\{v_i\}_{i=1\ldots N}$, respectively. Expressing each u_i in terms of the w_i's and each v_i in terms of the z_i's, we obtain

$$\lambda = \sum_{i,j} \beta_{ij} (w_i \otimes z_j).$$

Thus

$$\langle \lambda \,|\, \lambda \rangle = \sum_{i,j,k,m} \overline{\beta_{ij}} \beta_{km} \langle w_i \,|\, w_k \rangle \langle z_j \,|\, z_m \rangle = \sum_{i,j} |\beta_{ij}|^2 \geq 0,$$

and $\langle \lambda \,|\, \lambda \rangle = 0$ if and only if $\lambda = 0$.

Definition 24. *Let $\mathcal{H}_1$ and $\mathcal{H}_2$ be Hilbert spaces over $\mathbb{K}$. The* tensor product *$\mathcal{H}_1 \otimes \mathcal{H}_2$ is the completion of $(\mathcal{H}_1 \otimes \mathcal{H}_2)_{pre}$.*

Theorem 25. *If $(u_i)_{i\in\mathbb{N}}$ and $(v_i)_{i\in\mathbb{N}}$ are complete orthonormal systems in the Hilbert spaces $\mathcal{H}_1$ and $\mathcal{H}_2$ respectively, then $(u_i \otimes v_j)_{i,j\in\mathbb{N}}$ is a complete orthonormal system in $\mathcal{H}_1 \otimes \mathcal{H}_2$.*

Proof. $(u_i \otimes v_j)_{i,j\in\mathbb{N}}$ is orthonormal, so what remains to be shown is completeness, i.e. $\operatorname{span}(u_i \otimes v_j)_{i,j\in\mathbb{N}}$ is dense in $\mathcal{H}_1 \otimes \mathcal{H}_2$. It is sufficient to proof that $(\mathcal{H}_1 \otimes \mathcal{H}_2)_{\text{pre}}$ is contained in the closure of this span. Let $u \in \mathcal{H}_1$, $v \in \mathcal{H}_2$. We have

$$u = \sum_{i=1}^{\infty} \underbrace{\langle u_i \,|\, u \rangle}_{\alpha_i} u_i, \quad v = \sum_{i=1}^{\infty} \underbrace{\langle v_i \,|\, v \rangle}_{\beta_i} v_i.$$

Since $\sum_{i,j} |\alpha_i \beta_j|^2 = \sum_i |\alpha_i|^2 \sum_j |\beta_j|^2 < \infty$, the infinite series

$$\lambda := \lim_{N\to\infty} \sum_{i,j=1}^{N} \alpha_i \beta_j \, (u_i \otimes v_j)$$

converges in $\mathcal{H}_1 \otimes \mathcal{H}_2$, and

$$\left\| (u \otimes v) - \sum_{i,j=1}^{N} \alpha_i \beta_j \, (u_i \otimes v_j) \right\|^2 = \|u\|^2 \|v\|^2 - \sum_{i,j=1}^{N} |\alpha_i \beta_j|^2 \to 0.$$

□

We want to rigorously justify the "natural" isomorphism between L^2-spaces as follows.

Theorem 26. *Given two σ-finite measure spaces $(\Omega_1, \mathcal{A}_1, \mu_1)$, $(\Omega_2, \mathcal{A}_2, \mu_2)$ and assuming that the Hilbert spaces $L^2(\Omega_1, \mu_1)$ and $L^2(\Omega_2, \mu_2)$ are separable, there exists an isomorphism*

$$U : L^2(\Omega_1, \mu_1) \otimes L^2(\Omega_2, \mu_2) \to L^2(\Omega_1 \times \Omega_2, \mu_1 \otimes \mu_2)$$

so that

$$(Uf \otimes g)\,(x, y) = f(x)g(y) \quad \text{for all } f \in L^2(\Omega_1, \mu_1),\ g \in L^2(\Omega_2, \mu_2). \tag{B.1}$$

Proof. Let $(\varphi_i)_{i\in\mathbb{N}}$ and $(\psi_i)_{i\in\mathbb{N}}$ be complete orthonormal systems in $L^2(\Omega_1, \mu_1)$ and $L^2(\Omega_2, \mu_2)$, respectively. Then $(\varphi_i(x)\psi_j(y))_{i,j\in\mathbb{N}}$ is a complete orthonormal system in $L^2(\Omega_1 \times \Omega_2, \mu_1 \otimes \mu_2)$. The orthonormality is obvious, and the completeness can be seen as follows: let $h \in L^2(\Omega_1 \times \Omega_2, \mu_1 \otimes \mu_2)$ and suppose that for all i, j

$$\int_{\Omega_1 \times \Omega_2} \overline{\varphi_i(x)\psi_j(y)} h(x, y) \, \mathrm{d}x \, \mathrm{d}y = 0,$$

i.e.

$$\int_{\Omega_1} \overline{\varphi_i(x)} \left(\int_{\Omega_2} \overline{\psi_j(y)} h(x,y)\,\mathrm{d}y \right) \mathrm{d}x = 0.$$

Since $(\varphi_i)_i$ is complete, this means that up to a set of measure zero, the inner integral is zero for all $x \in \Omega_1$. Since $(\psi_i)_i$ is also complete, $h(x,y) = 0$ almost everywhere.

Now define U by

$$\left(U\varphi_i \otimes \varphi_j\right)(x,y) := \varphi_i(x)\psi_j(y).$$

U is a mapping between orthonormal systems and hence unitary. Note that we recover equation (B.1). □

The tensor product

$$\mathcal{H}_1 \otimes \cdots \otimes \mathcal{H}_n$$

of finitely many Hilbert spaces is a canonical extension of the above definitions.

In quantum mechanics, the Pauli exclusion principle states that multiple identical Fermions may not occupy the same state simultaneously. This translates to the antisymmetrization of wave functions.

Standard Example 27. *Let $(u_i)_{i\in\mathbb{N}}$ be a complete orthonormal system in the Hilbert space $\mathcal{H}$. For each permutation $\sigma \in S_n$, define an unitary operator given on basis elements of $\otimes^n\mathcal{H}$ by*

$$\sigma\left(u_{i_1} \otimes \cdots \otimes u_{i_n}\right) := u_{i_{\sigma(1)}} \otimes \cdots \otimes u_{i_{\sigma(n)}}.$$

*The n-*fold antisymmetric tensor product *$\wedge^n\mathcal{H}$ of $\mathcal{H}$ is the image of the orthogonal projection*

$$A_n := \frac{1}{n!} \sum_{\sigma\in S_n} \operatorname{sgn}(\sigma)\sigma.$$

Note that $\wedge^n\mathcal{H}$ is itself a Hilbert space. Set

$$u_{i_1} \wedge \cdots \wedge u_{i_n} := \sqrt{n!}\, A_n\left(u_{i_1} \otimes \cdots \otimes u_{i_n}\right),$$

then $(u_{i_1} \wedge \cdots \wedge u_{i_n})_{i_1<i_2<\cdots<i_n}$ is a complete orthonormal system in $\wedge^n\mathcal{H}$. In the special case where $\mathcal{H} = L^2(\Omega,\mu)$ and $(\Omega,\mathcal{A},\mu)$ is σ-finite, $\wedge^n\mathcal{H}$ is the set of all antisymmetric L^2-functions, i.e.

$$\begin{aligned} \wedge^n\mathcal{H} \simeq L^2(\Omega^n, \otimes^n\mu)_{anti} := \\ \big\{\varphi \in L^2(\Omega^n,\otimes^n\mu) \,:\, \varphi(\dots,x_i,\dots,x_j,\dots) \\ = -\varphi(\dots,x_j,\dots,x_i,\dots)\ \forall i \neq j \,\big\} \end{aligned}$$

It is obvious that σ is unitary as it permutes the orthonormal system $(u_{i_1} \otimes \cdots \otimes u_{i_n})_{i_1,\dots i_n\in\mathbb{N}}$. We show that σ is independent of the choice of $(u_i)_i$. Let $v_1,\dots,v_n \in \mathcal{H}$ and set $\alpha_{ij} := \langle u_i \,|\, v_j\rangle$. Then

$$\langle u_{i_1} \otimes \cdots \otimes u_{i_n} \,|\, v_1 \otimes \cdots \otimes v_n\rangle = \alpha_{i_1 1} \cdots \alpha_{i_n n}$$

and hence

$$\begin{aligned}\sigma\left(v_1 \otimes \cdots \otimes v_n\right) &= \sum_{i_1,\ldots,i_n} \alpha_{i_1 1} \cdots \alpha_{i_n n} \cdot u_{i_{\sigma(1)}} \otimes \cdots \otimes u_{i_{\sigma(n)}} \\ &= \sum_{i_1,\ldots,i_n} \alpha_{i_1 \sigma(1)} \cdots \alpha_{i_n \sigma(n)} \cdot u_{i_1} \otimes \cdots \otimes u_{i_2} \\ &= v_{\sigma(1)} \otimes \cdots \otimes v_{\sigma(n)}.\end{aligned}$$

It is easy to see that A_n is a linear, continuous, self-adjoint operator, and from $\sigma A_n = \operatorname{sgn}(\sigma) A_n$ we get $A_n^2 = A_n$, so A_n is an orthogonal projection. Note that

$$\operatorname{span}\{A_n\left(u_{i_1} \otimes \cdots \otimes u_{i_n}\right)\}_{i_1,\ldots,i_n \in \mathbb{N}}$$

is dense in $\wedge^n \mathcal{H}$ and $\left(A_n \sigma\right)\left(u_{i_1} \otimes \cdots \otimes u_{i_n}\right) = \operatorname{sgn}(\sigma) A_n\left(u_{i_1} \otimes \cdots \otimes u_{i_n}\right)$. We remark that for another orthonormal system $(v_i)_{i \in \mathbb{N}}$, the inner product has a special form:

$$\begin{aligned}&\langle v_1 \wedge \cdots \wedge v_n \,|\, u_1 \wedge \cdots \wedge u_n \rangle \\ &= n! \,\langle v_1 \otimes \cdots \otimes v_n \,|\, A_n(u_1 \otimes \cdots \otimes u_n) \rangle \\ &= \sum_{\sigma \in S_n} \operatorname{sgn}(\sigma) \prod_{\alpha=1}^{n} \left\langle v_\alpha \,|\, u_{\sigma(\alpha)} \right\rangle = \det \left\langle v_\alpha \,|\, u_\beta \right\rangle_{\alpha,\beta}.\end{aligned}$$

If $\mathcal{H} = L^2(\Omega, \mu)$, theorem 26 states

$$\otimes^n \mathcal{H} \simeq L^2(\Omega^n, \otimes^n \mu);$$

for each $\varphi \in L^2(\Omega^n, \otimes^n \mu)$, a basis expansion shows that

$$\left(A_n \varphi\right)\left(x_1, \ldots, x_n\right) = \frac{1}{n!} \sum_{\sigma \in S_n} \operatorname{sgn}(\sigma) \varphi\left(x_{\sigma(1)}, \ldots, x_{\sigma(n)}\right),$$

so $A_n \varphi$ is antisymmetric. Conversely, if φ is antisymmetric, then it's left invariant by A_n.

Proposition 28. *Let $(u_i)_{i \in \mathbb{N}}$ be a complete orthonormal system in the Hilbert space $\mathcal{H}$ and $U : \mathcal{H} \to \mathcal{H}$ an unitary operator. Then the operator (again denoted by U) given on basis elements of $\otimes^n \mathcal{H}$ by*

$$U\left(u_{i_1} \otimes \cdots \otimes u_{i_n}\right) := \left(U u_{i_1}\right) \otimes \cdots \otimes \left(U u_{i_n}\right)$$

is unitary and leaves $\wedge^n \mathcal{H}$ invariant.

Proof. It follows directly from the definitions that $U : \operatorname{span}\{u_{i_1} \otimes \cdots \otimes u_{i_n}\}_{i_1,\ldots,i_n} \to \operatorname{span}\{U u_{i_1} \otimes \cdots \otimes U u_{i_n}\}_{i_1,\ldots,i_n}$ is bijective and preserves norms. That is, U extends uniquely to an unitary operator $U : \otimes^n \mathcal{H} \to \otimes^n \mathcal{H}$. Furthermore $A_n U = U A_n$ as

$$\begin{aligned}&A_n U\left(u_{i_1} \otimes \cdots \otimes u_{i_n}\right) \\ &= \frac{1}{n!} \sum_{\sigma \in S_n} \operatorname{sgn}(\sigma) U u_{i_{\sigma(1)}} \otimes \cdots \otimes U u_{i_{\sigma(n)}} \\ &= U A_n\left(u_{i_1} \otimes \cdots \otimes u_{i_n}\right).\end{aligned}$$

From that it follows that the restriction U: $\wedge^n \mathcal{H} \to \wedge^n \mathcal{H}$ on the Hilbert space $\wedge^n \mathcal{H}$ is also unitary. □

We investigate vector-valued functions and their connection with tensor products.

Definition 29. *Let $(\Omega, \mathcal{A}, \mu)$ be a measure space and $\mathcal{H}'$ a separable Hilbert space. A function $f : \Omega \to \mathcal{H}'$ is called* measurable *if and only if $x \mapsto \langle y \,|\, f(x)\rangle$ is measurable for each $y \in \mathcal{H}'$. We set*

$$L^2(\Omega, \mu; \mathcal{H}') := \left\{ f : \Omega \to \mathcal{H}' \;:\; f \text{ measurable}, \int_\Omega \|f(x)\|^2 \,\mathrm{d}x < \infty \right\}.$$

We have to justify that $\|f(x)\|^2$ is measurable. Let $(u_i)_i$ be a complete orthonormal system in $\mathcal{H}'$. Then by definition, $x \mapsto \langle u_i \,|\, f(x)\rangle$ is measurable and hence also

$$x \mapsto \|f(x)\|^2 = \sum_i |\langle u_i \,|\, f(x)\rangle|^2 .$$

Note that since an inner product can be expressed by norms, $x \mapsto \langle f(x) \,|\, g(x)\rangle$ is also measurable for all $f, g \in L^2(\Omega, \mu; \mathcal{H}')$.

Proposition 30. *$L^2(\Omega, \mu; \mathcal{H}')$ given above is a Hilbert space with the inner product*

$$\langle f \,|\, g\rangle := \int_\Omega \langle f(x) \,|\, g(x)\rangle \,\mathrm{d}x.$$

Proof. Most results obtained for $L^2(\Omega, \mu)$ generalize literally to $L^2(\Omega, \mu; \mathcal{H}')$, especially the theorem by F. Riesz and E. Fischer which states the completeness of $L^2(\Omega, \mu)$. In this connection, e.g. note that given a sequence $(u_i)_i$ in $\mathcal{H}'$ with $\sum_{i=1}^\infty \|u_i\| < \infty$, the sequence of partial sums

$$s_n := \sum_{i=1}^n u_i$$

converges in $\mathcal{H}'$ since it is a Cauchy sequence:

$$\|s_{n+k} - s_n\| = \left\| \sum_{i=n+1}^{n+k} u_i \right\| \le \sum_{i=n+1}^{n+k} \|u_i\| \to 0 \quad \text{as } n \to \infty.$$

Thus we have generalized the well-known classical result on $\mathbb{C}$ that each absolutely convergent series is convergent. □

Theorem 31. *Let $(\Omega, \mathcal{A}, \mu)$ be a measure space such that $L^2(\Omega, \mu)$ is separable and let $\mathcal{H}'$ be a separable Hilbert space. Then there exists an isomorphism*

$$U : L^2(\Omega, \mu) \otimes \mathcal{H}' \to L^2(\Omega, \mu; \mathcal{H}')$$

such that

$$(Uf \otimes u)(x) = f(x)u \quad \text{for all } f \in L^2(\Omega, \mu),\ u \in \mathcal{H}'.$$

Proof. Choose complete orthonormal systems $(\varphi_i)_{i\in\mathbb{N}}$ and $(u_i)_{i\in\mathbb{N}}$ of $L^2(\Omega, \mu)$ and $\mathcal{H}'$, respectively. Obviously, $(\varphi_i u_j)_{i,j}$ is orthonormal; we show that it's also complete. Given $f \in L^2(\Omega, \mu; \mathcal{H}')$, let

$$h_j \in L^2(\Omega, \mu), \quad h_j(x) := \langle u_j \,|\, f(x)\rangle$$

and $\alpha_{ij} := \langle \varphi_i u_j \,|\, f \rangle = \langle \varphi_i \,|\, h_j \rangle$. Then by the theorem of monotone convergence,

$$\begin{aligned}\sum_{i,j} |\alpha_{ij}|^2 &= \sum_j \|h_j\|^2 = \int_\Omega \sum_j |h_j(x)|^2 \, \mathrm{d}x \\ &= \int_\Omega \sum_j |\langle u_j \,|\, f(x) \rangle|^2 \, \mathrm{d}x = \int_\Omega \|f(x)\|^2 \, \mathrm{d}x = \|f\|^2 < \infty\end{aligned}$$

and hence $\sum_{i,j=1}^\infty \alpha_{ij} \varphi_i u_j$ converges in $L^2(\Omega, \mu; \mathcal{H}')$. Furthermore,

$$\left\| f - \sum_{i,j=1}^N \alpha_{ij} \varphi_i u_j \right\|^2 = \|f\|^2 - \sum_{i,j=1}^N |\alpha_{ij}|^2 \to 0 \quad \text{as } N \to \infty.$$

Now define U by

$$(U \varphi_i \otimes u_j)(x) := \varphi_i(x) u_j,$$

which maps an orthonormal system to an orthonormal system and hence extends uniquely to an unitary operator. □

Appendix C

Second Quantization for Fermions

C.1 Introduction

The common term "Second Quantization" is somewhat misleading as it is just an efficient formalism for many-particle systems. Here we will consider fermions only (spin 1/2 particles). The spin-statistic theorem of relativistic quantum field theory states that fermions must be antisymmetric, i.e. the wave function changes sign under exchange of two identical particles.

C.2 Preliminaries

Let $\mathcal{H}$ be a Hilbert space and $\otimes^N\mathcal{H}$ the Hilbert space tensor product. $\wedge^N\mathcal{H}$ is the image of the orhogonal projection defined by

$$A_N\left(\varphi_1 \otimes \cdots \otimes \varphi_N\right) := \frac{1}{N!} \sum_{\sigma \in S_N} \operatorname{sgn}(\sigma) \varphi_{\sigma(1)} \otimes \cdots \otimes \varphi_{\sigma(N)}$$

(i.e. A_N is a linear, continuous, self-adjoint operator with $A_N^2 = A_N$). Physically speaking, $\wedge^N\mathcal{H}$ is the space where the antisymmetric many-particle function lives.

By definition, a Slater determinant is of the form

$$\varphi_1 \wedge \cdots \wedge \varphi_N := \sqrt{N!}\, A_N\left(\varphi_1 \otimes \cdots \otimes \varphi_N\right),$$

where $\varphi_1, \ldots \varphi_N \in \mathcal{H}$. If $\langle \varphi_\alpha \,|\, \varphi_\beta \rangle = \delta_{\alpha\beta}$, then it will be normalized.

Since $A_N^* = A_N$ and $A_N^2 = A_N$, the following holds:

$$\begin{aligned}
&\langle \varphi_1 \wedge \cdots \wedge \varphi_N \,|\, \psi_1 \wedge \cdots \wedge \psi_N \rangle \\
&= N! \,\langle \varphi_1 \otimes \cdots \otimes \varphi_N \,|\, A_N(\psi_1 \otimes \cdots \otimes \psi_N) \rangle \\
&= \sum_{\sigma \in S_N} \operatorname{sgn}(\sigma) \prod_{\alpha=1}^{N} \langle \varphi_\alpha \,|\, \psi_{\sigma(\alpha)} \rangle = \det \langle \varphi_\alpha \,|\, \psi_\beta \rangle_{\alpha,\beta}\,.
\end{aligned}$$

Remark: Let $(\varphi_i)_i$ be a complete orthonormal system of $\mathcal{H}$. Then

$$(\varphi_{i_1} \wedge \cdots \wedge \varphi_{i_N})_{i_1<i_2<\cdots<i_N}$$

is a complete orthonormal system of $\wedge^N\mathcal{H}$.

C.3 Creation and annihilation operators

Let $(\varphi_i)_i$ be a complete orthonormal system in the Hilbert space $\mathcal{H}$. When appropriate, we set $|i\rangle = \varphi_i$. Furthermore, let $\varphi, \psi \in \mathcal{H}$ and assume that $\psi_1, \ldots, \psi_N \in \mathcal{H}$ are orthonormal. We define a creation operator by

$$a^\dagger_\varphi \, \psi_1 \wedge \cdots \wedge \psi_N := \varphi \wedge \psi_1 \wedge \cdots \wedge \psi_N,$$

extending linearly. The adjoint "annihilation" operator is then

$$a_\varphi \, \psi_1 \wedge \cdots \wedge \psi_N := \sum_{\alpha=1}^{N} (-1)^{\alpha+1} \langle \varphi \,|\, \psi_\alpha \rangle \, \psi_1 \wedge \ldots \psi_{\alpha-1} \wedge \psi_{\alpha+1} \cdots \wedge \psi_N.$$

This can be seen from the column expansion theorem for determinants:

$$\begin{aligned}
&\left\langle \psi_1 \wedge \cdots \wedge \psi_N \,|\, a^\dagger_\varphi \, \chi_1 \wedge \cdots \wedge \chi_{N-1} \right\rangle \\
&= \sum_{\gamma=1}^{N} (-1)^{\gamma+1} \langle \psi_\gamma \,|\, \varphi \rangle \det \langle \psi_\alpha \,|\, \chi_\beta \rangle_{\alpha\neq\gamma,\beta} \\
&= \left\langle a_\varphi \, \psi_1 \wedge \cdots \wedge \psi_N \,|\, \chi_1 \wedge \cdots \wedge \chi_{N-1} \right\rangle .
\end{aligned}$$

From a physical point of view, these operators increase/decrease the particle number by one. We write $a^\dagger_i := a^\dagger_{\varphi_i}$ and $a_i := a_{\varphi_i}$. The anticommutator brackets yield

$$\{a_\varphi, a_\psi\} = 0, \quad \left\{a^\dagger_\varphi, a^\dagger_\psi\right\} = 0, \quad \left\{a_\varphi, a^\dagger_\psi\right\} = \langle \varphi \,|\, \psi \rangle .$$

The "occupation number operator" for the state φ,

$$\hat{n}_\varphi := a^\dagger_\varphi a_\varphi,$$

derives its name from the following property:

$$\hat{n}_{\varphi_j} \varphi_{i_1} \wedge \cdots \wedge \varphi_{i_N} = \begin{cases} 1 & j \in \{i_1, \ldots, i_N\} \\ 0 & \text{otherwise} \end{cases}$$

Given the operator $T : \mathcal{H} \to \mathcal{H}$, we want to rewrite

$$\tilde{T} = \sum_{\alpha=1}^{N} T_\alpha \qquad (T_\alpha \text{ acting on the } \alpha\text{-th particle})$$

in terms of creation and annihilation operators.

$$\begin{aligned}
&\left(\sum_{\alpha=1}^{N} |\varphi\rangle_\alpha\langle\chi|_\alpha\right)\psi_1\wedge\cdots\wedge\psi_N\\
&=\sum_{\alpha=1}^{N}\langle\chi\,|\,\psi_\alpha\rangle\,(-1)^{\alpha+1}a_\varphi^\dagger\;\psi_1\wedge\ldots\psi_{\alpha-1}\wedge\psi_{\alpha+1}\cdots\wedge\psi_N\\
&=a_\varphi^\dagger a_\chi\;\psi_1\wedge\cdots\wedge\psi_N,\quad\text{i.e.}\\
&\sum_{\alpha=1}^{N}|\varphi\rangle_\alpha\langle\chi|_\alpha=a_\varphi^\dagger a_\chi,
\end{aligned}$$

so we have

$$\tilde{T}=\sum_{\alpha=1}^{N}\sum_{i,j}\langle i\,|\,T\,j\rangle\,|i\rangle_\alpha\langle j|_\alpha=\sum_{i,j}\langle i\,|\,T\,j\rangle\,a_i^\dagger a_j.$$

In order to handle two-particle interactions, we first define pair creation and annihilation operators by

$$\begin{aligned}
&a_{\varphi\wedge\psi}^\dagger:=a_\varphi^\dagger a_\psi^\dagger,\qquad\text{extending to}\quad a_{\varphi_1\wedge\psi_1+c\,\varphi_2\wedge\psi_2}^\dagger=a_{\varphi_1\wedge\psi_1}^\dagger+c\,a_{\varphi_2\wedge\psi_2}^\dagger\\
&a_{\varphi\wedge\psi}:=\left(a_{\varphi\wedge\psi}^\dagger\right)^*=a_\psi a_\varphi.
\end{aligned}$$

Now use $\delta_{kj}=\left\{a_k,a_j^\dagger\right\}$ to get

$$\begin{aligned}
\sum_{\alpha\neq\beta}|i\rangle_\alpha|j\rangle_\beta\langle k|_\alpha\langle l|_\beta&=\sum_{\alpha\neq\beta}|i\rangle_\alpha\langle k|_\alpha|j\rangle_\beta\langle l|_\beta\\
&=\sum_{\alpha,\beta}|i\rangle_\alpha\langle k|_\alpha|j\rangle_\beta\langle l|_\beta-\delta_{kj}\sum_\alpha|i\rangle_\alpha\langle l|_\alpha\\
&=a_i^\dagger a_k a_j^\dagger a_l-a_i^\dagger\left\{a_k,a_j^\dagger\right\}a_l=-a_i^\dagger a_j^\dagger a_k a_l\\
&=a_{i\wedge j}^\dagger a_{k\wedge l}.
\end{aligned}$$

Given a pair operator V, applying the above result yields

$$\begin{aligned}
\tilde{V}&:=\frac{1}{2}\sum_{\alpha\neq\beta}V_{\alpha,\beta}\\
&=\frac{1}{2}\sum_{\alpha\neq\beta}\sum_{i,j,k,l}\langle i\otimes j\,|\,V\;k\otimes l\rangle\,|i\rangle_\alpha|j\rangle_\beta\langle k|_\alpha\langle l|_\beta\\
&=\frac{1}{2}\sum_{i,j,k,l}\langle i\otimes j\,|\,V\;k\otimes l\rangle\,a_{i\wedge j}^\dagger a_{k\wedge l}\\
&=\frac{1}{2}\sum_{i<j,\,k<l}\langle i\otimes j-j\otimes i\,|\,V\;(k\otimes l-l\otimes k)\rangle\,a_{i\wedge j}^\dagger a_{k\wedge l}\\
&=\sum_{i<j,\,k<l}\langle i\wedge j\,|\,V\;k\wedge l\rangle\,a_{i\wedge j}^\dagger a_{k\wedge l},
\end{aligned}$$

that is, given a complete orthonormal system $(\chi_i)_i$ in $\wedge^2\mathcal{H}$,

$$\tilde{V}=\sum_{i,j}\langle\chi_i\,|\,V\chi_j\rangle\,a_{\chi_i}^\dagger a_{\chi_j}.$$

Let's investigate the special case

$$V = |\chi\rangle\langle\chi|, \quad \chi \in \wedge^2\mathcal{H}:$$

$$\tilde{V} = \sum_i \langle \chi_i \,|\, \chi\rangle \, a^\dagger_{\chi_i} \sum_j \langle \chi \,|\, \chi_j\rangle \, a_{\chi_j} = a^\dagger_\chi a_\chi \equiv \hat{n}_\chi.$$

Note that the pair operators have bosonic character. A short computation shows that

$$\left[a^\dagger_{i\wedge j}, a^\dagger_{k\wedge l}\right] = 0,$$

and, taking the adjoints,

$$[a_{i\wedge j}, a_{k\wedge l}] = 0.$$

Using

$$\left[a_i, a^\dagger_k a^\dagger_l\right] = a_i a^\dagger_k a^\dagger_l - a^\dagger_k a^\dagger_l a_i = \delta_{ik} a^\dagger_l - \delta_{il} a^\dagger_k,$$

we get

$$\left[a_{i\wedge j}, a^\dagger_{k\wedge l}\right] = \left[a_j a_i, a^\dagger_k a^\dagger_l\right] = \delta_{ik} a_j a^\dagger_l - \delta_{il} a_j a^\dagger_k + \delta_{jk} a^\dagger_l a_i - \delta_{jl} a^\dagger_k a_i.$$

Given an unitary operator $U : \mathcal{H} \to \mathcal{H}$, we obtain an unitary operator (also denoted by U) acting on $\wedge^N\mathcal{H}$ by

$$U\left(\psi_1 \wedge \cdots \wedge \psi_N\right) := \left(U\psi_1\right) \wedge \cdots \wedge \left(U\psi_N\right).$$

From

$$\begin{aligned}\left(U^* a^\dagger_{U\varphi} U\right)\left(\psi_1 \wedge \cdots \wedge \psi_N\right) &= U^*\left(U\varphi \wedge U\psi_1 \wedge \cdots \wedge U\psi_N\right) \\ &= \varphi \wedge \psi_1 \wedge \cdots \wedge \psi_N\end{aligned}$$

we get

$$U^* a^\dagger_{U\varphi} U = a^\dagger_\varphi$$

for all $\varphi \in \mathcal{H}$, and, taking the adjoint,

$$U^* a_{U\varphi} U = a_\varphi.$$

The canonical generalization to p-body creation and annhihilation operators is as follows:

$$\begin{aligned}a^\dagger_{i_1\wedge\cdots\wedge i_p + c\cdot j_1\wedge\cdots\wedge j_p} &:= a^\dagger_{i_1}\cdots a^\dagger_{i_p} + c\cdot a^\dagger_{j_1}\cdots a^\dagger_{j_p}, \\ a_{i_1\wedge\cdots\wedge i_p + c\cdot j_1\wedge\cdots\wedge j_p} &:= \left(a^\dagger_{i_1\wedge\cdots\wedge i_p + c\cdot j_1\wedge\cdots\wedge j_p}\right)^* \\ &= a_{i_p}\cdots a_{i_1} + \overline{c}\cdot a_{j_p}\cdots a_{j_1}.\end{aligned}$$

Given $\chi \in \wedge^p\mathcal{H}$, we set

$$\hat{n}_\chi := a^\dagger_\chi a_\chi.$$

This relates to the single-particle occupation numbers as follows:

$$\hat{n}_{i_1\wedge\cdots\wedge i_p} = a^\dagger_{i_1}\cdots a^\dagger_{i_p} a_{i_p}\cdots a_{i_1} = \hat{n}_{i_1}\cdots\hat{n}_{i_p}.$$

For the last expression we have used the anticommutator relations. Let $(\chi_i)_i$ be a complete orthonormal system in $\wedge^p\mathcal{H}$ and fix the particle number $N \geq p$ (that is, we operate on $\wedge^N\mathcal{H}$). Then

$$\sum_i \hat{n}_{\chi_i} = \binom{N}{p} \cdot \mathrm{id}_{\wedge^N\mathcal{H}}.$$

This can be seen by a Slater determinant expansion.

We reproduce an interesting result concerning commutator relations. Let

$$S = \sum_{i,j} s_{ij}\, a_i^\dagger a_j, \quad T = \sum_{i,j} t_{ij}\, a_i^\dagger a_j,$$

then an explicit calculation shows that

$$[S,T] = \sum_{i,j} [s,t]_{ij}\; a_i^\dagger a_j.$$

In particular, if s commutes with t then S and T commute as well. This is a rigorous proof of the intuitive fact that commuting single-particle operators also commute when applied to a many-particle system.

C.4 L^2 wave functions

In physics, the most widely used Hilbert spaces are L^2 spaces. (And in fact, each finite-dimensional or separable Hilbert space is isomorphic to a L^2 space.) In this chapter we rewrite the creation and annihilation operators in terms of integrals, which are the building blocks of L^2-spaces.

Given a measure space $(\Omega, \mathcal{A}, \mu)$ and $\mathcal{H} = L^2(\Omega, \mathbb{C})$, the wedge product is similar to the antisymmetrized product space, i.e.

$$\begin{aligned} \wedge^N\mathcal{H} \simeq L^2_{\mathrm{anti}}(\Omega^N, \mathbb{C}) := \\ \big\{ \Psi \in L^2(\Omega^N, \mathbb{C}) \;:\; \Psi(\dots, x_i, \dots, x_j, \dots) \\ = \Psi(\dots, x_j, \dots, x_i, \dots)\ \forall i \neq j \ \big\}. \end{aligned}$$

The creation and annihilation operators are given by

$$\begin{aligned} \big(a_\varphi^\dagger \Psi\big)(x_1, \dots, x_{N+1}) = \frac{1}{\sqrt{N+1}} \sum_{\alpha=1}^{N+1} (-1)^{\alpha+1} \varphi(x_\alpha) \times \\ \Psi(x_1, \dots, x_{\alpha-1}, x_{\alpha+1}, \dots, x_{N+1}) \quad \forall \varphi \in \mathcal{H},\ \Psi \in \wedge^N\mathcal{H} \end{aligned}$$

and

$$\left(a_\varphi \Psi\right)(x_1, \dots, x_{N-1}) = \sqrt{N} \int_\Omega \overline{\varphi(x)} \Psi(x, x_1, \dots, x_{N-1})\, \mathrm{d}x.$$

This can be directly derived from the definition. Let $\Psi = \psi_1 \wedge \cdots \wedge \psi_N$.

$$\begin{aligned}
\left(a_\varphi^\dagger \Psi\right) &= \varphi \wedge \psi_1 \wedge \cdots \wedge \psi_N \\
&= (-1)^N \psi_1 \wedge \cdots \wedge \psi_N \wedge \varphi \\
&= (-1)^N \frac{1}{\sqrt{N+1}} \sum_{\alpha=1}^{N+1} \varphi(x_\alpha) \frac{1}{\sqrt{N!}} \sum_{\substack{\sigma \in S_{N+1} \\ \sigma(\alpha)=N+1}} \operatorname{sgn}(\sigma) \times \\
&\qquad \psi_{\sigma(1)}(x_1) \cdots \psi_{\sigma(\alpha-1)}(x_{\alpha-1}) \cdot \psi_{\sigma(\alpha+1)}(x_{\alpha+1}) \cdots \psi_{\sigma(N+1)}(x_{N+1}) \\
&= (-1)^N \frac{1}{\sqrt{N+1}} \sum_{\alpha=1}^{N+1} \varphi(x_\alpha) \frac{1}{\sqrt{N!}} (-1)^{N+1-\alpha} \sum_{\tau \in S_N} \operatorname{sgn}(\tau) \times \\
&\qquad \psi_{\tau(1)}(x_1) \cdots \psi_{\tau(\alpha-1)}(x_{\alpha-1}) \cdot \psi_{\tau(\alpha)}(x_{\alpha+1}) \cdots \psi_{\tau(N)}(x_{N+1}) \\
&= \frac{1}{\sqrt{N+1}} \sum_{\alpha=1}^{N+1} (-1)^{\alpha+1} \varphi(x_\alpha) \Psi(x_1, \ldots, x_{\alpha-1}, x_{\alpha+1}, \ldots, x_{N+1}).
\end{aligned}$$

An explicit calculation based on

$$\left\langle \Psi \,|\, a_\varphi^\dagger \Phi \right\rangle = \left\langle a_\varphi \Psi \,|\, \Phi \right\rangle$$

gives the formula for $a_\varphi \Psi$.

Let $\chi = \varphi \wedge \psi \in \wedge^2 \mathcal{H}$, then by definition $a_\chi = a_\psi a_\varphi$, so

$$\begin{aligned}
&(a_\chi \Psi)(x_1, \ldots, x_{N-2}) \\
&\quad = \sqrt{N-1} \int_\Omega \overline{\psi(y)} \left(a_\varphi \Psi\right)(y, x_1, \ldots, x_{N-2}) \, \mathrm{d}y \\
&\quad = \sqrt{N(N-1)} \int_\Omega \int_\Omega \frac{1}{2} \left[\overline{\varphi(x)\psi(y) - \varphi(y)\psi(x)}\right] \Psi(x, y, x_1, \ldots, x_{N-2}) \, \mathrm{d}x \, \mathrm{d}y \\
&\quad = \binom{N}{2}^{\frac{1}{2}} \int_\Omega \int_\Omega \overline{\chi(x,y)} \Psi(x, y, x_1, \ldots, x_{N-2}) \, \mathrm{d}x \, \mathrm{d}y.
\end{aligned}$$

A short calculation shows that

$$\begin{aligned}
\left(a_\chi^\dagger \Psi\right)(x_1, \ldots, x_{N+2}) = \binom{N+2}{2}^{-\frac{1}{2}} \sum_{\substack{\alpha,\beta=1 \\ \alpha<\beta}}^{N+2} (-1)^{\alpha+\beta+1} \chi(x_\alpha, x_\beta) \times \\
\Psi(x_1, \ldots, x_{\alpha-1}, x_{\alpha+1}, \ldots, x_{\beta-1}, x_{\beta+1}, \ldots, x_{N+2}).
\end{aligned}$$

This can easily be generalized to p-body creation and annihilation operators, for example, for $\chi \in \wedge^p \mathcal{H}$ and $\Psi \in \wedge^N \mathcal{H}$,

$$\left(a_\chi \Psi\right)(x_1, \ldots, x_{N-p}) = \binom{N}{p}^{\frac{1}{2}} \int_{\Omega^p} \overline{\chi(x'_1, \ldots, x'_p)} \Psi(x'_1, \ldots, x'_p, x_1, \ldots, x_{N-p}) \, \mathrm{d}x'_1 \ldots \mathrm{d}x'_p.$$

Appendix D

An Algebraic Approach

D.1 Basic setup

In this chapter we start from a purely algebraic approach to antisymmetrized many-particle Hilbert spaces.

Definition 32. *Let $K \in \mathbb{N}_{\geq 1}$ and $\mathcal{H}$ be a K-dimensional complex Hilbert space, where we denote an orthonormal basis by $|s\rangle, s = 1, \ldots, K$. The* antisymmetrized many-particle Hilbert space *is defined by*

$$\wedge\mathcal{H} := \operatorname{span}\{|S\rangle \,:\, S \subseteq \{1,\ldots,K\}\} = \left\{ \sum_S \alpha_S |S\rangle \,:\, \alpha_S \in \mathbb{C} \right\},$$

i.e. the subsets of $\{1,\ldots,K\}$ serve as orthonormal basis. For $p \in \{0,1,\ldots,K\}$, the antisymmetrized p-particle Hilbert space *is*

$$\wedge^p\mathcal{H} := \operatorname{span}\{|S\rangle \,:\, S \subseteq \{1,\ldots,K\},\ |S| = p\}.$$

Note that $\mathcal{H} = \wedge^1\mathcal{H}$ and $\wedge^p\mathcal{H}$ is naturally embedded in $\wedge\mathcal{H}$.

Given two disjoint subsets $S = \{i_1,\ldots,i_n\}$ and $T = \{i_{n+1},\ldots,i_m\}$ with $i_1 < i_2 < \cdots < i_n$ and $i_{n+1} < \cdots < i_m$, let σ be the permutation of $\{1,\ldots,m\}$ such that $i_{\sigma(1)} < i_{\sigma(2)} < \cdots < i_{\sigma(m)}$. Set

$$\operatorname{sgn}(S,T) := \begin{cases} \operatorname{sgn}(\sigma), & \text{if } S \cap T = \emptyset \\ 0, & \text{otherwise} \end{cases}$$

An immediate consequence is the following:

$$\operatorname{sgn}(S,T) = (-1)^{|S|\cdot|T|} \operatorname{sgn}(T,S) \quad \forall\, S,T \subseteq \{1,\ldots,K\}.$$

Definition 33. *Define so-called* creation operators *acting on basis vectors of $\wedge\mathcal{H}$ by $a^\dagger_{|S\rangle}|T\rangle := \operatorname{sgn}(S,T)\,|S \cup T\rangle$, extending linearly in $|S\rangle$ and $|T\rangle$. The adjoint $a_\varphi := \left(a^\dagger_\varphi\right)^*$ ($\varphi \in \wedge\mathcal{H}$) is called* annihilation operator *and is antilinear in φ. Explicitly,*

$$a_{|S\rangle}|T\rangle = \begin{cases} \operatorname{sgn}(S, T\backslash S)\,|T\backslash S\rangle, & \textit{if } S \subseteq T \\ 0, & \textit{otherwise} \end{cases}$$

Furthermore, set

$$n_\varphi := a^\dagger_\varphi a_\varphi \quad \textit{and} \quad c_\varphi := a_\varphi a^\dagger_\varphi.$$

Corollary 34. *For all $S, T \subseteq \{1, \ldots, K\}$ we have*

$$n_{|S\rangle}|T\rangle = \begin{cases} |T\rangle, & S \subseteq T \\ 0, & \text{otherwise} \end{cases} \quad \text{and} \quad c_{|S\rangle}|T\rangle = \begin{cases} |T\rangle, & T \cap S = \emptyset \\ 0, & \text{otherwise} \end{cases}$$

so $n_{|S\rangle}$ and $c_{|S\rangle}$ are projections, and the corresponding subspaces are orthogonal if $S \neq \emptyset$. Note that $n_{|\emptyset\rangle} = c_{|\emptyset\rangle} = \mathrm{id}_{\wedge\mathcal{H}}$.
For all $i \in \{1, \ldots, K\}$,

$$n_{|i\rangle} + c_{|i\rangle} = \mathrm{id}_{\wedge\mathcal{H}}.$$

An explicit (tedious) calculation using basic facts about permutations shows the following relations:

Proposition 35. *For all $S, T \subseteq \{1, \ldots, K\}$,*

$$\begin{aligned}
a^\dagger_{|S\rangle}|T\rangle &= (-1)^{|S|\cdot|T|}\, a^\dagger_{|T\rangle}|S\rangle, \\
a^\dagger_{|S\rangle}a^\dagger_{|T\rangle} &= \mathrm{sgn}(S,T)\, a^\dagger_{|S\cup T\rangle}, \\
a_{|S\rangle}a^\dagger_{|T\rangle} &= (-1)^{|S|\cdot|T|}\, a^\dagger_{|T\rangle}a_{|S\rangle} \quad \text{if} \quad S \cap T = \emptyset, \\
a_{|S\rangle}a^\dagger_{|T\rangle} &= \mathrm{sgn}(S\cap T, T\backslash S)\,\mathrm{sgn}(S\cap T, S\backslash T)\, a_{|S\backslash T\rangle}\, a^\dagger_{|T\backslash S\rangle}\, c_{|S\cap T\rangle}, \\
a^\dagger_{|T\rangle}a_{|S\rangle} &= (-1)^{|S\cap T|\cdot|S\Delta T|}\,\mathrm{sgn}(S\cap T, T\backslash S)\,\mathrm{sgn}(S\cap T, S\backslash T)\, a^\dagger_{|T\backslash S\rangle}\, a_{|S\backslash T\rangle}\, n_{|S\cap T\rangle}.
\end{aligned}$$

Corollary 36. *Let $\varphi \in \wedge^p\mathcal{H}$ and $\psi \in \wedge^q\mathcal{H}$. Then*

$$\begin{aligned}
\left[a^\dagger_\varphi, a^\dagger_\psi\right] = 0, \quad [a_\varphi, a_\psi] = 0 \quad &\text{if } pq \text{ is even}, \quad \text{and} \\
\left\{a^\dagger_\varphi, a^\dagger_\psi\right\} = 0, \quad \{a_\varphi, a_\psi\} = 0 \quad &\text{if } pq \text{ is odd}.
\end{aligned}$$

Let $S, T \subseteq \{1, \ldots, K\}$ such that $S \cap T = \emptyset$. Then

$$\begin{aligned}
\left[a_{|S\rangle}, a^\dagger_{|T\rangle}\right] = 0 \quad &\text{if } |S|\cdot|T| \text{ is even}, \\
\left\{a_{|S\rangle}, a^\dagger_{|T\rangle}\right\} = 0 \quad &\text{if } |S|\cdot|T| \text{ is odd}.
\end{aligned}$$

D.2 Invariance under single-particle base changes

Definition 37. *For any unitary operator $U \in \mathcal{B}(\mathcal{H})$, let $U^\otimes$ be the unitary operator acting on $\wedge\mathcal{H}$ by*

$$U^\otimes|i_1, \ldots, i_p\rangle := a^\dagger_{U|i_1\rangle} \cdots a^\dagger_{U|i_p\rangle}|\emptyset\rangle$$

for all $1 \leq i_1 < \cdots < i_p \leq K$.

Note that this corresponds to a renaming of the basis elements $|1\rangle, \ldots, |K\rangle$ of $\mathcal{H}$.

Proposition 38. *Let $U \in \mathcal{B}(\mathcal{H})$ be unitary. Then for all $\varphi \in \wedge\mathcal{H}$,*

$$\left(U^\otimes\right)^* a^\dagger_{U^\otimes\varphi} U^\otimes = a^\dagger_\varphi,$$

and – taking the adjoint –

$$\left(U^\otimes\right)^* a_{U^\otimes\varphi} U^\otimes = a_\varphi.$$

D.3 Reduced density matrices

We can now re-define reduced density matrices, acting on the whole many-particle space $\wedge\mathcal{H}$.

Definition 39. *Given* $\Psi \in \wedge\mathcal{H}$, $\|\Psi\| = 1$, *its* reduced density matrix *is the linear operator* γ_Ψ *acting on* $\wedge\mathcal{H}$ *by*

$$\langle \chi \,|\, \gamma_\Psi \varphi \rangle := \langle a_\varphi \Psi \,|\, a_\chi \Psi \rangle = \left\langle \Psi \,|\, a_\varphi^\dagger a_\chi \Psi \right\rangle .$$

As an immediate consequence, γ_Ψ is positive semidefinite and self-adjoint.

Proposition 40. *Let additionally* $\Psi \in \wedge^N\mathcal{H}$ *for fixed* N. *Then* $\operatorname{tr}\gamma_\Psi = 2^N$, *and for any* p, γ_Ψ *leaves* $\wedge^p\mathcal{H}$ *invariant, with* $\operatorname{tr}_{\wedge^p\mathcal{H}}\gamma_\Psi = \binom{N}{p}$.

Proof. Just note that for all T, $\sum_{S\subseteq\{1,\dots,K\}} n_{|S\rangle}|T\rangle =$ "number of subsets of T" $= 2^{|T|}$, and $\sum_{|S|=p} n_{|S\rangle}|T\rangle = \binom{|T|}{p}$. □

For $\varphi = \sum_{S\subseteq\{1,\dots,K\}} \alpha_S|S\rangle$ ($\alpha_S \in \mathbb{C}$) we set $\overline{\varphi} := \sum_{S\subseteq\{1,\dots,K\}} \overline{\alpha_S}|S\rangle$, i.e. the complex conjugate of the coefficients in the standard basis expansion.

Let again be $\Psi \in \wedge\mathcal{H}$, $\|\Psi\| = 1$, and define a linear operator $\hat{\Psi}$ given on basis elements by $\hat{\Psi}|S\rangle := a_{|S\rangle}\Psi$. Note that due to the antilinearity of the annihilation operator, we have $\hat{\Psi}\varphi = a_{\overline{\varphi}}\Psi$. Now observe the following: for all $S, T \subseteq \{1,\dots,K\}$,

$$\begin{aligned}\left\langle T \,|\, \hat{\Psi} S \right\rangle = \langle T \,|\, a_{|S\rangle}\Psi\rangle = \left\langle a_{|S\rangle}^\dagger T \,|\, \Psi \right\rangle = (-1)^{|S|\cdot|T|} \left\langle a_{|T\rangle}^\dagger S \,|\, \Psi \right\rangle \\ = (-1)^{|S|\cdot|T|} \langle S \,|\, a_{|T\rangle}\Psi\rangle = (-1)^{|S|\cdot|T|} \langle a_{|T\rangle}\overline{\Psi} \,|\, S\rangle = (-1)^{|S|\cdot|T|} \left\langle \hat{\overline{\Psi}} T \,|\, S \right\rangle .\end{aligned}$$

If $\Psi \in \wedge^N\mathcal{H}$, the above term is nonzero only if $|S| + |T| = N$. For N odd we thus have $(-1)^{|S|\cdot|T|} = 1$. It follows that $\left(\hat{\Psi}\right)^* = \hat{\overline{\Psi}}$. γ_Ψ can now be rewritten in terms of $\hat{\Psi}$:

$$\langle S \,|\, \gamma_\Psi T\rangle = \langle a_{|T\rangle}\Psi \,|\, a_{|S\rangle}\Psi\rangle = \langle a_{|S\rangle}\overline{\Psi} \,|\, a_{|T\rangle}\overline{\Psi}\rangle = \left\langle S \,|\, \hat{\Psi}\left(\hat{\Psi}\right)^* T \right\rangle ,$$

that is, $\gamma_\Psi = \hat{\Psi}\left(\hat{\Psi}\right)^*$. In particular, the eigenvalues satisfy $\lambda_i(\gamma_\Psi) = \sigma_i\left(\hat{\Psi}\right)^2$ and $\operatorname{tr}\gamma_\Psi = \left\|\hat{\Psi}\right\|_{\text{fro}}^2$.

D.4 Particle-hole duality

Definition 41. *The* dual operator $*$ *acting on* $\wedge\mathcal{H}$ *is the antilinear operator*

$$*(\varphi) := a_\varphi|\mathbb{1}\rangle \quad \textit{with} \quad |\mathbb{1}\rangle \equiv |1, 2, \dots, K\rangle.$$

A short calculation shows that $\left\{n_{|i\rangle} - n_{|j\rangle}, *\right\} = 0$ for all i, j.

D.5 Ground states of interaction Hamiltonians

Fix $p \in \{0, 1, \ldots, K\}$ and let h be a self-adjoint linear operator acting on $\wedge^p \mathcal{H}$. Introduce the self-adjoint linear operator $H := \sum_{S,T} \langle S \,|\, hT \rangle \, a^\dagger_{|S\rangle} a_{|T\rangle}$ acting on $\wedge^N \mathcal{H}$ for fixed $N \geq p$. Our goal is to find the smallest eigenvalue of H, i.e. the minimum of $\langle \Psi \,|\, H\Psi \rangle$, $\Psi \in \wedge^N \mathcal{H}, \|\Psi\| = 1$. Here comes in the reduced density matrix:

$$\begin{aligned} \langle \Psi \,|\, H\Psi \rangle &= \sum_{S,T} \langle S \,|\, hT \rangle \left\langle \Psi \,|\, a^\dagger_{|S\rangle} a_{|T\rangle} \Psi \right\rangle = \sum_{S,T} \langle S \,|\, hT \rangle \, \langle T \,|\, \gamma_\Psi S \rangle \\ &= \sum_S \langle S \,|\, h\gamma_\Psi S \rangle = \mathrm{tr}_{\wedge^p \mathcal{H}} \left(h\gamma_\Psi \right). \end{aligned}$$

Now consider the special case $p = 2$ and $h = \sum_{|S|=2} \lambda_S |S\rangle\langle S|$ with given $\lambda_S \in \mathbb{R}$. Then $H = \sum_{|S|=2} \lambda_S n_{|S\rangle}$, and the standard basis elements $T \subseteq \{1, \ldots, K\}$ with $|T| = N$ are exactly the eigenvectors of H:

$$H|T\rangle = \sum_{S \subseteq T, |S|=2} \lambda_S |T\rangle.$$

Thus we try to solve

$$\min_{|T|=N} \sum_{S \subseteq T, |S|=2} \lambda_S.$$

Define a real symmetric matrix $A = (a_{ij})$ and a vector $x \in \{0,1\}^K$ by

$$a_{ij} = \begin{cases} \frac{1}{2}\lambda_{\{i,j\}}, & i \neq j \\ 0, & \text{otherwise} \end{cases} \qquad \text{and} \qquad x_i = \begin{cases} 1, & i \in T \\ 0, & \text{otherwise} \end{cases}$$

then $\langle T \,|\, HT \rangle = \langle x \,|\, Ax \rangle$. This results in the following integer quadratic programming problem on $\{0,1\}^K$:

$$\min x^T A x \quad \text{subject to} \quad c^T x = N, \quad c = (1, \ldots, 1)^T.$$

Note that we can without loss of generality assume that A is positive definite since $x^T A x = x^T \left(A + \lambda I_K \right) x - \lambda N$ for all $\lambda \in \mathbb{R}$.

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