Quasi-pinning and entanglement
in the lithium isoelectronic series

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Abstract

The Pauli exclusion principle gives an upper bound of 1 on the natural occupation numbers. Recently there has been an intriguing amount of theoretical evidence that there is a plethora of additional generalized Pauli restrictions or (in)equalities, of kinematic nature, satisfied by these numbers \cite{1}. Here for the first time a numerical analysis of the nature of such constraints is effected in real atoms. The inequalities are nearly saturated, or quasi-pinned. For rank-six and rank-seven approximations for lithium, the deviation from saturation is smaller than the lowest occupancy number. For a rank-eight approximation we find well-defined families of saturation conditions.

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1 Introduction

The natural occupation numbers, arranged in the customary decreasing order $\lambda_1 \geq \lambda_2 \geq \cdots$ fulfill $0 \leq \lambda_i \leq 1$, for all $i$ — thus allowing no more than one electron in each quantum state. Forty years ago Borland and Dennis [2] observed for the rank-six approximation of a three-electron system, whose state space is here denoted $\lambda^3 \mathcal{H}_6$, that the six occupation numbers satisfy the additional constraints $\lambda_r + \lambda_7-r = 1$, where $r \in \{1, 2, 3\}$, allowing exactly one electron in the natural orbitals $r$ and $7-r$. Moreover,

$$\lambda_4 \leq \lambda_5 + \lambda_6. \quad (1)$$

The proofs are given in [3]. Thanks to outstanding work by Klyachko and others in the last few years, actually solving the pure state $N$-representability problem for the one-body reduced density matrix [1], the pattern of the occupation numbers has received renewed attention. Large sets of inequalities for the eigenvalues of this matrix, widely generalizing (1), have been established. We note that, while the pure $N$-representability problem for the two-body reduced density matrix remains unsolved, the ensemble $N$-representability problem for this matrix is now solved [4].

A recent article [5] proposes to give an analytic study of the Klyachko conditions by means of a toy model: a one-dimensional system of three spinless fermions confined to a harmonic well, interacting with each other through Hooke-type forces. A series formula for the occupation numbers in terms of the coupling was found.

The tantalizing suggestion in [5] is that the inequalities are nearly saturated in the ground state [i.e., in equations like Eq. (1) the equality almost holds]: this is the “quasi-pinning” phenomenon, which points to a deep hold on the kinematics of the system. Schilling et al [5] state “... it is likely extremely challenging to use numerical methods to distinguish between genuinely pinned and mere quasi-pinned states”.

In the work we report here, we have taken up this challenge by studying the ground state of lithium-like ions, starting from scratch with an elementary configuration interaction (CI) method, up to a rank-eight approximation (here, the rank equals the number of basis functions in setting up the CI expansion). This procedure serves a twofold purpose. First, we shall study whether the conclusions of Schilling et al. [5] are valid for realistic systems, too. There now exists a profound measure of quantum entanglement for three-fermion systems in rank six [6]. A second goal of the present work is therefore to adapt this measure to our physical spin-partitioned systems, contrasting the results with the information on entanglement traditionally provided by the $\lambda_i$.

In the present paper we shall present our analysis and results as follows.

Section 2 gives a simple introduction to the problem at hand. We discuss in some detail the one- and two-body matrices in the relatively trivial approximation of rank five to the lithium-like ground states $\lambda^5 \mathcal{H}_5$.

In Section 3 we broach the subject of entanglement for our systems. This will allow us to discuss subsequently the information-theoretic meaning of pinning and quasi-pinning.

Section 4 deals with the first non-trivial approximation to the three-electron system (of...
rank six). We use two different basis sets, and the comparison of the results turns out to be very instructive.

Section 5 analyzes the more complicated cases of rank seven and eight approximations. Finally, Section 6 summarizes our conclusion.

We emphasize that the calculated energies merely are used to provide information on the quality of our approximations and, accordingly, on how accurate our calculated occupation numbers are, including our conclusions with regard to the quasi-pinning hypothesis. Our goal is to grapple with its impact on chemistry, and to investigate the negative correlation between it and entanglement. Thus we refrain completely from gaining extra accuracy of machine calculations at the price of losing insight.

In two appendices we give some additional mathematical information. The first discusses the ideas behind the Klyachko constraints in ordinary quantum chemical language. The second gives the proof of an estimate that we shall present in Section 5.

Finally, throughout this work we use Hartree atomic units.

2 The simplest case: a rank-five configuration for lithium-alikes

Consider a system of $N$ electrons and $M$ spin orbitals $\{\varphi_i(x)\}_{i=1}^M$, each being a product of a spatial orbital and a spinor. We employ the standard quantum-chemical notation $x := (r, \varsigma)$ and use the notational convention: $\varphi_i(x) := \phi_i(r) \varsigma$, with $\varsigma \in \{\uparrow, \downarrow\}$. The number of configurations $N_c$ that can be constructed from $M$ spin orbitals for $N$ electrons and $M - N$ holes is

$$N_c = \binom{M}{N},$$

which grows as a factorial with $M$. Here, we assume that we have identified a set of basis functions, largely under the guidance of the physical or chemical intuition, that provides an accurate description of the system of our interest. For the $N$-electron wave function, we use wave functions made of normalized Slater determinants,

$$|\Psi\rangle = \sum_J C_J [\varphi_{J(1)} \cdots \varphi_{J(N)}].$$

With the exterior algebra notation, this becomes

$$[\varphi_1 \varphi_2 \cdots \varphi_N] := \frac{1}{\sqrt{N!}} |\varphi_1\rangle \wedge |\varphi_2\rangle \wedge \cdots \wedge |\varphi_N\rangle.$$

In general, we assume that the $\varphi_i$ have been orthonormalized, although we occasionally relate them to non-orthogonal orbitals by

$$\varphi_i(x) = \sum_{j=1}^L R_{ij} \psi_j(r, \varsigma). \tag{2}$$
We define the following energy integrals:

\[ \kappa_{mn} := \int \frac{\varphi_m(x) \varphi_n(x)}{|r|} dx, \quad \pi_{mn} := -\frac{1}{2} \int \nabla^2_r \varphi_m(x) \varphi_n(x) dx \]

\[ \iota_{mnop} := \int \frac{\varphi_m(x_1) \varphi_n(x_1) \varphi_o(x_2) \varphi_p(x_2)}{|r_1 - r_2|} dx_1 dx_2; \]

\[ K_{mn} := \int \frac{\psi_m(x) \psi_n(x)}{|r|} dx, \quad P_{mn} := -\frac{1}{2} \int \nabla^2_r \psi_m(x) \psi_n(x) dx \]

\[ \Upsilon_{mnop} := \int \frac{\psi_m(x_1) \psi_n(x_1) \psi_o(x_2) \psi_p(x_2)}{|r_1 - r_2|} dx_1 dx_2. \] (3)

From one set of integrals one can construct other sets by means of the relations \( \kappa = (R \otimes R) K \), \( \pi = (R \otimes R) P \) and \( \iota = (R \otimes R \otimes R \otimes R) \Upsilon \), where \( R \) is the transformation matrix in (2).

2.1 A simple starting configuration

Given its low ionization potential (\( \simeq 0.198 \) au), it is natural to explore radial configurations of the open-shell lithium atom with a single-determinant composition of (a) two restricted helium-like spin orbitals — in turn motivated by the classical analysis by Shull and Löwdin [8] of the natural orbitals for spin singlet states of He — and (b) one hydrogen-like, in a suitably general sense. Specifically, in such a single configuration we use the Kellner Ansatz for the helium-like functions,

\[ \psi_1(\alpha, r) = \sqrt{\frac{\alpha^3}{\pi}} e^{-\alpha r}. \]

For the spinor of the hydrogen-like function we have arbitrarily chosen \( \downarrow \). For the spatial orbital, typical textbook calculations can be used for the \( s \)-orbital in the \( L \)-shell:

\[ \psi^s_3(\gamma, r) = \frac{1}{4} \sqrt{\frac{\gamma^3}{2\pi}} L_1^1(\gamma r) e^{-\gamma r/2} = \frac{1}{4} \sqrt{\frac{\gamma^3}{2\pi}} (2 - \gamma r) e^{-\gamma r/2}. \]

Moreover, we consider also the following functions,

\[ \psi^p_3(\gamma, r) = \frac{1}{4} \sqrt{\frac{\gamma^5}{6\pi}} r e^{-\gamma r/2} \quad \text{or} \quad \psi^d_3(\gamma, r) = \frac{1}{8} \sqrt{\frac{\gamma^7}{45\pi}} r^2 e^{-\gamma r/2}. \]

With these functions we obtain better results than with \( \psi^s_3 \); see Table [1]. The better approximation among the three, which includes \( \phi^p_3 \), leads to a total energy that equals 99.19% of the “exact” value. Comparing to the Hartree–Fock (HF) energy given by the “best” Slater determinant, the error is less than 0.2% — much more satisfactory than the Kellner approximation for helium.

For higher \( Z \) in the lithium series, the accuracy naturally improves, although we shall not discuss this issue further here. Notice instead that the \( R \)-matrix mentioned above is just
| Conf          | Energy (au) | α   | γ   |
|--------------|-------------|-----|-----|
| “exact”      | −7.478060   | −   | −   |
| HF           | −7.432727   | −   | −   |
| \[ψ_1↑ψ_1↑ψ_{3↓}\] | −7.393597   | 2.679747 | 1.868327 |
| \[ψ_1↑ψ_1↑ψ_{3↓}\] | −7.416163   | 2.691551 | 1.892738 |
| \[ψ_1↑ψ_1↑ψ_{3↓}\] | −7.417919   | 2.686435 | 1.274552 |

Table 1: The exact, HF and variational energy of Li in a single-determinant configuration. Note the more substantial screening of the outer electron by the inner ones when including \(ϕ_3^p\) in the basis.

a Gram–Schmidt orthonormalization matrix, i.e.,

\[
\begin{pmatrix}
ϕ_1↑ \\
ϕ_1↓ \\
ϕ_{3↓}
\end{pmatrix} = R \begin{pmatrix}
ψ_1↑ \\
ψ_1↓ \\
ψ_{3↓}
\end{pmatrix}, \quad \text{where} \quad R = \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & -\frac{1}{\sqrt{1-|⟨ψ_1|ψ_3⟩|^2}} & \frac{1}{\sqrt{1-|⟨ψ_1|ψ_3⟩|^2}}
\end{pmatrix}.
\]

In order to simplify the presentation, we shall not give below the explicit forms of such matrices.

### 2.2 The rank-five computation

We obtain the rank-five approximation by using two helium-like one-particle wave functions and one hydrogen-like. Still being guided by [8], for the former we add the following function of the set (orthonormal on the ordinary space):

\[
δ_n(r) := D_n \sqrt{\frac{α^3}{π}} L_{n-1}^2(2αr)e^{-αr}; \quad n = 1, 2, \ldots
\]

where \(D_n^{-2} = \binom{n-1}{2}\), and the associated Laguerre polynomials \(L_n^\zeta\) are as defined in [9]. We have thus

\[
δ_2(α, r) := \sqrt{\frac{α^3}{3π}} L_1^2(2αr)e^{-αr}.
\]

We shall adopt the following notation for an orthonormalized basis set of the restricted spin-orbital type:

\[
\begin{align*}
|1⟩ & := ϕ_{3↓}, \quad |2⟩ := δ_1↓, \quad |3⟩ := δ_2↓, \quad |4⟩ := δ_1↑, \quad |5⟩ := δ_2↑; \\
\end{align*}
\]

where

\[
\begin{pmatrix}
|1⟩ \\
|2⟩ \\
|3⟩ \\
|4⟩ \\
|5⟩
\end{pmatrix} = R \begin{pmatrix}
ψ_{3↓} \\
δ_1↓ \\
δ_2↓ \\
δ_1↑ \\
δ_2↑
\end{pmatrix}.
\]
With rank five, one has in principle $10 = \binom{5}{2}$ Slater determinants. However, since the adopted Hamiltonian is independent of the spin coordinates, only pure spin states are physically meaningful. Obviously, there are only six determinants which are eigenvectors of the operator $S_z$, namely,

$$[124], \ [134], \ [125], \ [135], \ [234], \ [235].$$  \tag{4}

The total spin operator $S^2$ can be written as $S_- S_+ + S_z + S_z^2$. It is clear that the states in (4) are eigenstates of the operator $S_z$ (and consequently of $S_z^2$). However, it is less clear whether they are eigenstates of $S_- S_+$, too. It is easy to show that the wave function

$$|\Psi\rangle = A[124] + B[134] + C[125] + D[135] + E[234] + F[235]$$

satisfies

$$S_- S_+ |\Psi\rangle - |\Psi\rangle \propto (B - C)([134] + [1'23] + [125]),$$

where $|1'\rangle$ is a spin-up counterpart of $|1\rangle$. Therefore $S_- S_+ |\Psi\rangle = |\Psi\rangle$ and $S^2 |\Psi\rangle = \frac{3}{4} |\Psi\rangle$ if and only if $B = C$.

Throughout the remaining parts of this paper, we have used a similar approach to identify those spin-adapted combinations of Slater determinants, that are eigenfunctions to $S^2$ and, accordingly, are not “spin-contaminated” states.

Finally, the normalized wave function is written as

$$A[124] + B[125] + B[134] + D[135] + E[234] + F[235], \tag{5}$$

with $|A|^2 + 2|B|^2 + |D|^2 + |E|^2 + |F|^2 = 1.$

With rows and columns indexed by $\{1, \ldots, 5\}$, the corresponding one-body density matrix is expressed by the matrix

$$
\begin{pmatrix}
|A|^2 + 2|B|^2 + |D|^2 & BE^* + DF^* & -AE^* - BF^* & 0 & 0 \\
B^*E + D^*F & |A|^2 + |B|^2 + |D|^2 + |F|^2 & AB^* + BD^* & 0 & 0 \\
-A^*E - B^*F & A^*B + B^*D & |B|^2 + |D|^2 + |E|^2 + |F|^2 & 0 & 0 \\
0 & 0 & 0 & A^*B + B^*D + E^*F & |B|^2 + |D|^2 + |F|^2
\end{pmatrix}.
$$

In our case,

$$\rho_1(x_1, x_1') = 3 \int \Psi(x_1, x_2, x_3) \Psi^*(x_1', x_2, x_3) \, dx_2 \, dx_3.$$ 

We can now conclude that only combinations of the form $|[abc]\rangle\langle[dbe]|$ will contribute (where the order of $a$, $b$, and $c$, as well as of $d$, $b$, and $c$ can be changed when simultaneously taking the appropriate signs into account). For instance, $|[124]\rangle\langle[125]|$ contributes with $AB^*$ to the 45 matrix entry; $|[134]\rangle\langle[234]|$ contributes with $-BE^*$ to the 12 entry, and so on. Note that the trace of this matrix is equal to 3, as it should be.\footnote{This is a result of the global multiplication by the factor equal to the number of electrons; as well as a division by $3!$, coming from the appropriate constant of the determinants; and the fact that each multiplication of two Slater terms contributes twice.}

6
We thus have $\lambda_1 + \lambda_2 + \lambda_3 = 2$ and $\lambda_4 + \lambda_5 = 1$ for the natural occupation numbers; the primes in the notation are due to them being not yet in decreasing order.

By definition, in the basis of natural orbitals $\{|\alpha_i\rangle\}$, the one-body density matrix is diagonal: $\rho_1 = \sum_{i=1}^{5} \lambda_i |\alpha_i\rangle \langle \alpha_i|$, already assuming that the occupation numbers are arranged in decreasing order by interchanging $\lambda_3$ with $\lambda_4$. Therefore, it is evident that a strong selection rule applies: we can rewrite the wave function for a three-electron system in rank five in terms of only two configurations:

$$|\Psi\rangle_{3,5} = a[\alpha_1 \alpha_2 \alpha_3] + d[\alpha_1 \alpha_4 \alpha_5]; \quad |a|^2 + |d|^2 = 1, \quad \lambda_2 = \lambda_3 = |a|^2 \geq |d|^2 = \lambda_4 = \lambda_5. \quad (6)$$

Through this example we have given a simple proof of a theorem stated by Coleman [10]. A more sophisticated proof is found in [11, Cor. 2].

### 2.3 Spectral analysis of the $n$-body and $n$-hole density matrices on $\wedge^3 \mathcal{H}_5$

According to the Schmidt–Carlson–Keller duality [10], when applied to a three-electron system, the nonzero eigenvalues as well as their multiplicities are the same for the one- and the two-body matrices, i.e.,

$$\rho_2 = \sum_{i=1}^{5} \lambda_i |\omega_i\rangle \langle \omega_i|,$$

where $c_j |\omega_j\rangle := 3 \int \Psi(x_1, x_2, x_3) \alpha_j^* (x_3) \, dx_3$ with $|c_j|^2 = \lambda_j$.

Thus, the eigenvectors of the two-body matrix associated to the wave function (6) are given by

$$|\omega_1\rangle = a[\alpha_2 \alpha_3] + d[\alpha_4 \alpha_5], \quad |\omega_2\rangle = [\alpha_1 \alpha_3], \quad |\omega_3\rangle = [\alpha_1 \alpha_2], \quad |\omega_4\rangle = [\alpha_1 \alpha_5], \quad |\omega_5\rangle = [\alpha_1 \alpha_4].$$

For a system of $N$ particles and $M - N$ holes, the $n$-hole matrix is hermitian and antisymmetric in each set of subindices, similar to what is the case for the $n$-particle matrix. Additionally, it satisfies the normalization conditions and sum rules,

$$\text{Tr} \eta_n = \binom{M-N}{n}; \quad \int \eta_n \, dx_n = \frac{M - N - n}{n} \eta_{n-1}.$$

In the natural orbital basis, the one-hole matrix becomes

$$\eta_1 = \sum_{i=1}^{M} (1 - \lambda_i) |\alpha_i\rangle \langle \alpha_i|,$$

i.e., $M - N = 5 - 3 = 2$ in our case; while the two-hole matrix is the $Q$-matrix of lore, which for the lithium in the rank-five approximation is

$$\eta_2 = \sum_{i=1}^{5} \mu_i |h_i\rangle \langle h_i| = |h_1\rangle \langle h_1|,$$

where $\mu_i = 0$ if $|\omega_i\rangle$ is a single determinant and otherwise $\mu_i = \lambda_i$. Here, $|h_1\rangle := d[\alpha_2 \alpha_3] + a[\alpha_4 \alpha_5]$. Note that $\eta_2$ is idempotent:

$$\eta_2^2 = (|h_1\rangle \langle h_1|)^2 = \eta_2 \quad \text{because} \quad \langle h_1| h_1\rangle = 1.$$
3 Preliminary discussion of entanglement in $\wedge^3 \mathcal{H}_6$

We consider two different approaches for obtaining six-rank approximations for lithium-like ions. One is to work in a scheme of fully restricted spin orbitals. Then, the sixth molecular orbital is chosen as $\psi_3^p \uparrow$. An alternative is to include $\delta_3 \downarrow$ instead.

For convenience, we use the notation

$$
\begin{pmatrix}
|1\rangle \\
|2\rangle \\
|3\rangle \\
|4\rangle \\
|5\rangle \\
|6\rangle
\end{pmatrix}
= R
\begin{pmatrix}
\delta_1 \uparrow \\
\delta_1 \downarrow \\
\psi_3^p \downarrow \\
\delta_2 \downarrow \\
\delta_2 \uparrow \\
\psi_3^p \uparrow
\end{pmatrix};
$$

$$
\begin{pmatrix}
|1\rangle \\
|2\rangle \\
|3\rangle \\
|4\rangle \\
|5\rangle \\
|6\rangle
\end{pmatrix}
= R
\begin{pmatrix}
\delta_1 \uparrow \\
\delta_1 \downarrow \\
\psi_3^p \downarrow \\
\delta_2 \downarrow \\
\delta_2 \uparrow \\
\delta_3 \downarrow
\end{pmatrix};
$$

(7)

respectively, for the two cases.

Before discussing the two approaches in detail in the next section, it is useful to first discuss the relations between chemistry and entanglement in each case, in the light of [6] and of the quite recent analysis of universal subspaces for fermionic systems [11]. Without doubt, the search for an entanglement measure for multipartite systems is among the most important challenges facing quantum information theory [12]. For three fermions, there have been some attempts to generalize the Schmidt decomposition, widely used in bipartite systems. Both [6] and [11] focus on rank-six descriptions, since these are the lowest non-trivial ones for tripartite systems.

Neither of the choices made in those papers is well adapted to the needs of chemistry, the first being too general, and the second too restrictive. The measure of entanglement proposed in [6] on the basis of cubic Jordan algebra theory does not take account of spin-partitioning. A wave function $|\Phi\rangle$ belonging to the abstract twenty-dimensional Hilbert space $\wedge^3 \mathcal{H}_6$ is considered. Given an ordered basis of $\wedge^3 \mathcal{H}_6$ and

$$
|\Phi\rangle = \sum_{1 \leq i < j < k \leq 6} c_{ijk} [ijk],
$$

(8)

its amount of entanglement is analyzed in terms of the absolute value of the expression

$$
\mathcal{T} := 4 \{ [\text{Tr}(M_1 M_2) - \mu \nu]^2 - 4 \text{Tr}(M_1^# M_2^#) + 4 \mu \det M_1 + 4 \nu \det M_2 \}
$$

with $0 \leq |\mathcal{T}| \leq 1$,

where the twenty amplitudes of (8) are arranged in two $3 \times 3$ matrices and two scalars,

$$
M_1 := \begin{pmatrix}
c_{156} & -c_{146} & c_{145} \\
c_{256} & -c_{246} & c_{245} \\
c_{356} & -c_{346} & c_{345}
\end{pmatrix},

M_2 := \begin{pmatrix}
c_{234} & -c_{134} & c_{124} \\
c_{235} & -c_{135} & c_{125} \\
c_{236} & -c_{136} & c_{126}
\end{pmatrix},

\mu := c_{123}
\text{ and } \nu := c_{456}.
$$

Here, $M^#$ denotes the adjugate of a matrix $M$, such that $MM^# = M^#M = (\det M)I$. Under this measure, non-trivial tripartite entanglement can take place in two inequivalent ways: those with $|\mathcal{T}| \neq 0$ and those with $|\mathcal{T}| = 0$ — provided that then a pertinent dual
wavefunction \( \tilde{\Phi} \) is different from zero. Although both cases exhibit genuine tripartite entanglement (they are neither separable nor biseparable), there is no unitary transformation relating the two types of states. The lowest configuration of the energy with the basis set \( \{ \psi^3_3 \downarrow, \psi^3_3 \uparrow, \delta^1_1 \uparrow, \delta^1_1 \downarrow, \delta^2_1 \uparrow, \delta^2_1 \downarrow \} \) considered in the first part of this chapter results in a \( T \)-measure of entanglement equal to zero. In contrast, the wave function constructed from \( \{ \psi^3_3 \downarrow, \delta^1_1 \uparrow, \delta^1_1 \downarrow, \delta^2_2 \uparrow, \delta^2_2 \downarrow, \delta^3_3 \downarrow \} \) results in \( T \)-entanglement equal to \( 2.57 \times 10^{-6} \) (admittedly small, due to quasi-pinning, as we explain later); which in particular means that entanglement-wise pinned states and unpinned ones are mutually disconnected.

On the other hand, the framework of the analysis in [11] is applicable for only the first of the two configurations mentioned in (7).

4 Rank-six approximations

4.1 Choosing two configurations

It is readily seen that for the first basis set in (7), out of \( 20 = \binom{6}{3} \) Slater determinants there are nine eigenfunctions of \( S_z \) with eigenvalue \( \downarrow \),

\[
[123], [124], [245], [345], [236], [346], [134], [246], [235].
\]

The first six Slater determinants are eigenvectors of \( S^2 \), which also is true for the combinations

\[
[134] + [246] \quad \text{and} \quad [235] - [134].
\]

Consider thus the following wavefunctions

\[
A[123] + B([235] - [134]) + E[124] + F[245] + D[345] + G[236] + H[346] + I([246] + [134]).
\]

The notation corresponds to that of (5), with, however, a numbering change. It is easy to see that the corresponding one-body matrix has the following spin structure

\[
\rho_1 = \rho_1^\uparrow \oplus \rho_1^\downarrow
\]

whereby, with respective indices \( \{1, 5, 6\} \) and \( \{2, 3, 4\} \),

\[
\rho_1^\uparrow = \begin{pmatrix} |A|^2 + |B|^2 + |E|^2 + |I|^2 & \ast & \ast \\ \ast & |B|^2 + |D|^2 + |F|^2 & \ast \\ \ast & \ast & |G|^2 + |H|^2 + |I|^2 \end{pmatrix}, \quad \text{Tr} \rho_1^\uparrow = 1;
\]

\[
\rho_1^\downarrow = \begin{pmatrix} |A|^2 + |B|^2 + |E|^2 + |G|^2 + |I|^2 & \ast & \ast \\ \ast & |A|^2 + 2|B|^2 + |D|^2 + |G|^2 + |H|^2 + |I|^2 & \ast \\ \ast & \ast & |B|^2 + |D|^2 + |E|^2 + |F|^2 + |H|^2 + 2|I|^2 \end{pmatrix}, \quad \text{Tr} \rho_1^\downarrow = 2.
\]

For the second basis system in (7), among the 20 Slater determinants there are now twelve eigenfunctions of the operator \( S^z \) with eigenvalue \( \downarrow \), namely,

\[
[123], [124], [245], [345], [134], [235], [146], [256], [136], [356], [126], [456].
\]
| Rank | Energy   | $\alpha$ | $\gamma$ |
|------|----------|----------|----------|
| 3    | $-7.417919$ | $2.686435$ | $1.274552$ |
| 5    | $-7.431181$ | $2.711177$ | $1.304903$ |
| 6$^a$| $-7.431827$ | $2.674424$ | $1.319161$ |
| 6$^b$| $-7.431639$ | $2.712166$ | $1.323417$ |
| 7    | $-7.445443$ | $2.772402$ | $1.336274$ |
| 8    | $-7.454889$ | $2.767562$ | $1.331108$ |

Table 2: Variational energy of Li in a CI picture for different approximation rank.

Table 3: Occupation numbers from ranks five to eight for lithium wave functions.

Here, we shall not write explicitly the general wavefunction that can be constructed from those and that does not contain any spin contamination.

Table 2 presents the results for the energy and screening parameters, with 6$^a$ and 6$^b$ respectively denoting the first and second case in (7). In the table we have also included the results for higher-rank approximations.

Table 3 gives the results for the natural orbital occupancy numbers.

The (four) Klyachko inequalities for a three-electron system in a rank-six configuration read

$$\lambda_1 + \lambda_6 \leq 1, \quad \lambda_2 + \lambda_5 \leq 1, \quad \lambda_3 + \lambda_4 \leq 1; \quad 0 \leq D := \lambda_5 + \lambda_6 - \lambda_4.$$  

However, one must have $\sum_{i=1}^{6} \lambda_i = 3$. As a consequence of this, the first inequalities become saturated (the Borland–Dennis identities), and there is only one inequality left for further examination. Note that we can formulate this as

$$\lambda_1 + \lambda_2 \leq 1 + \lambda_3.$$  

Before analyzing $D$, which is the main subject in this subsection, we emphasize that the Borland–Dennis identities are fulfilled within our numerical accuracy. Also, they imply that in the natural orbital basis every Slater determinant is composed of three orbitals $[\alpha_i \alpha_j \alpha_k]$, each belonging to one of three different sets, say

$$\alpha_i \in \{\alpha_1, \alpha_6\}, \quad \alpha_j \in \{\alpha_2, \alpha_5\} \quad \text{and} \quad \alpha_k \in \{\alpha_3, \alpha_4\};$$

\footnote{With our method it is necessary to reach rank seven in order to obtain part of the (radial) correlation energy. It is well known that the best HF ground state for Li is given by an unrestricted determinant.}
that is $\lambda^3 H_6$ splits with a section equal to $H_2^{\otimes 3}$ for a system of three fermions with spin.

*Quasi-pinning* is the property of $D$ being extremely close to zero. Within our calculation $6^b$, we find

$$0 \leq D = \lambda_5 + \lambda_6 - \lambda_4 = 2.1465 \times 10^{-5}.$$  \hfill (12)

This value of $D$ is slightly smaller than the lowest occupation number, $D/\lambda_6 \approx 0.97$. $D$ cannot exceed $\lambda_6$, because otherwise $\lambda_5 > \lambda_4$. More remarkable is that for the restricted determinant case $6^a$ one has $D$ of order $10^{-12}$, i.e., 0 within numerical accuracy.

The inequality (11) together with the decreasing ordering rule define a polytope (Fig. 1) in the space of the occupancy numbers.

Figure 1: (Color online) Polytope defined by the expression $\lambda_1 + \lambda_2 \leq 1 + \lambda_3$, subject to the condition $1 \geq \lambda_1 \geq \lambda_2 \geq \lambda_3 \geq 0$. The saturation condition $\lambda_1 + \lambda_2 = 1 + \lambda_3$ is satisfied by the points on one of the faces of the polytope, the one with edges $\lambda_2 = \lambda_3$ for $\lambda_1 = 1$ and $\lambda_1 = 1 - \lambda_2$ for $\lambda_3 = 0$. The single determinant state is placed at the corner $\lambda_1 = \lambda_2 = \lambda_3 = 1$ of the polytope. The physical ground states appear to be (close to) saturated

So far, a number of findings and conclusions can be emphasized:

- The energy computed via the restricted basis set $6^a$ is (marginally) better than that obtained via $6^b$.

- Quasi-pinning is “strict” for $6^a$ — in fact we do have *pinning* — and “lax” for $6^b$. Indeed, equation (12) is still remarkable in absolute terms. But it just means that if the system is close to a vertex, it is close to a face.

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• Both states are truly entangled — neither separable nor biseparable. However, the $\mathcal{T}$-measure of entanglement vanishes for $6^a$, while $\mathcal{T} \neq 0$ for $6^b$. Thus, in some sense the latter is “more entangled” than the former. In fact, referring to the original notation (9), for the case $6^a$, we have the expressions:

$$M_1 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & -c_{246} & c_{245} \\ 0 & -c_{346} & c_{345} \end{pmatrix}, \quad M_2 = \begin{pmatrix} 0 & -c_{134} & c_{124} \\ c_{235} & 0 & 0 \\ c_{236} & 0 & 0 \end{pmatrix}, \quad \mu = c_{123} \text{ and } \nu = 0,$$

and hence

$$\mathcal{T} = 4\{[\text{Tr}(M_1M_2) - \mu\nu]^2 - 4\text{Tr}(M_1^#M_2^#) + 4\mu\det M_1 + 4\nu\det M_2]\} = 0.$$

For the case $6^b$, again referring to the original notation (9), we deal with

$$M_1 = \begin{pmatrix} 0 & -c_{146} & 0 \\ c_{256} & 0 & c_{245} \\ 0 & 0 & c_{345} \end{pmatrix}, \quad M_2 = \begin{pmatrix} 0 & -c_{134} & c_{124} \\ c_{235} & 0 & 0 \\ c_{236} & 0 & 0 \end{pmatrix}, \quad \mu = c_{123} \text{ and } \nu = c_{456},$$

and hence

$$\mathcal{T} = 4\{[\text{Tr}(M_1M_2) - \mu\nu]^2 - 4\text{Tr}(M_1^#M_2^#) + 4\mu\det M_1 + 4\nu\det M_2]\} = 4\{-c_{146}c_{235} - c_{134}c_{256} + c_{126}c_{345} - c_{123}c_{456}\}^2 - 4(c_{134}c_{146}c_{235}c_{256} - c_{126}c_{146}c_{235}c_{245} - c_{126}c_{134}c_{256}c_{345} + 4c_{123}c_{146}c_{256}c_{345} + 4c_{456}c_{126}c_{134}c_{235}\} = -2.5718 \times 10^{-6}.$$

• It is accordingly natural to conjecture, as already done in [5], that pinning leads to qualitative differences in multipartite entanglement, and quasi-pinning correlates negatively with entanglement.

• Computing entanglement by means of the standard Jaynes entropy — $\sum_i \lambda_i \ln \lambda_i$ we obtain for the restricted configuration $2.05 \times 10^{-2}$ and $1.99 \times 10^{-2}$ for the partially unrestricted one. Admittedly, these two values are close but nevertheless it would seem to contrarily indicate that $6^b$ is “less entangled” than $6^a$. In total, this suggests that there is a need to identify genuine multipartite measures of entanglement. The recent proposal [13] looks enticing in this respect.

• When the fourth inequality saturates ($D = 0$), a strong selection rule like (6) applies, namely, the number of Slater determinants reduces to three:

$$|\Psi\rangle_{3,6} = a[\alpha_1\alpha_2\alpha_3] + b[\alpha_1\alpha_4\alpha_5] + c[\alpha_2\alpha_4\alpha_6]. \quad (13)$$

It should be clear that $\{\alpha_1, \alpha_2, \alpha_4\}$, $\{\alpha_3, \alpha_5, \alpha_6\}$ respectively span the spaces on which $\rho_1^\uparrow$, $\rho_1^\downarrow$ in (10) act. The natural occupation numbers for this wavefunction are of the form:

$$\lambda_1 = |a|^2 + |b|^2, \quad \lambda_2 = |a|^2 + |c|^2, \quad \lambda_3 = |a|^2, \quad \lambda_4 = |b|^2 + |c|^2. \quad \lambda_5 = |b|^2, \quad \lambda_6 = |c|^2.$$
When employing a restricted basis set, there is no loss of information in working with the wave function (13). Even in the general case, at rank six simultaneous variation of orbitals and coefficients is still a tempting proposition for the lithium series, in view of the following. The possible loss of information when projecting the total wave function onto this subspace of pinned states has been computed [14]. Given a wave function $|\Phi\rangle \in \wedge^3 H_6$, and letting $P$ be the projection operator onto the subspace spanned by the Slater determinants $[\alpha_1\alpha_2\alpha_3]$, $[\alpha_1\alpha_4\alpha_5]$ and $[\alpha_2\alpha_4\alpha_6]$, we have the following upper and lower bounds for this projection,

$$1 - \frac{1 + 2\xi}{1 - 4\xi} D \leq \|P\Phi\|_2^2 \leq 1 - \frac{1}{2} D,$$

provided $\xi := 3 - \lambda_1 - \lambda_2 - \lambda_3 < \frac{1}{4}$. Within our calculations the lower bound is larger than 99.997%. Presumably, by dint of astute variation tactics one could obtain extremely good values for the energy with just three Slater terms.

Finally, returning to the article [11], the authors there correctly argue that their treatment of universal subspaces gives an alternative proof for the Klyachko representability conditions on $\wedge^3 H_6$. Conversely, the above gives an independent proof of the assertions in [11], for the same case.

### 4.2 Reduced matrices on pinned $\wedge^3 H_6$

As in the rank-five case, the one-body and one-hole matrices read $\rho_1 = \sum_{i=1}^6 \lambda_i |\alpha_i\rangle \langle \alpha_i|$ and $\eta_1 = \sum_{i=1}^6 (1 - \lambda_i) |\alpha_i\rangle \langle \alpha_i|.

The two-body and two-hole matrices are, respectively, written as

$$\rho_2 = \sum_{i=1}^6 \lambda_i |\omega_i\rangle \langle \omega_i| \quad \text{and} \quad \eta_2 = \sum_{i=1}^6 \mu_i |h_i\rangle \langle h_i| = \sum_{i \in \{1,2,4\}} \lambda_j |h_j\rangle \langle h_j|,$$

with $|\omega_i\rangle := \frac{3}{\sqrt{\lambda_i}} |\alpha_i\rangle \langle \Psi|$, and

$$|h_1\rangle = \frac{1}{\sqrt{\lambda_1}} (b[\alpha_2\alpha_3] + a[\alpha_4\alpha_5]), \quad |h_2\rangle = \frac{1}{\sqrt{\lambda_2}} (c[\alpha_1\alpha_3] + a[\alpha_4\alpha_6]),$$

$$|h_4\rangle = \frac{1}{\sqrt{\lambda_4}} (c[\alpha_1\alpha_5] + b[\alpha_2\alpha_6]);$$

note that $|h_j\rangle = |\omega_j\rangle$ for $i = 3, 5, 6$ correspond to single determinants. Moreover, $\eta_2^2 = \eta_2$.

### 4.3 Z-dependency of the quasi-pinning

The dependence of the inequality (12) on the atomic number of the nucleus deserves some extra discussion. The first occupation number will grow as the atomic charge in the nucleus increases. Fig. [2] features the evolution of the saturation when $Z$ takes values in $\{3, \ldots, 12\}$. The most relevant measure is $D/\lambda_6$, which (mostly) decreases with $Z$. This means that the numerical distance between $\lambda_5$ and $\lambda_4$ — or between $\lambda_2$ and $\lambda_3$ — is rapidly decreasing with $Z$. 13
5 Klyachko theory in higher-rank approximations

5.1 A rank-seven approximation

We choose the basis set

\[
\begin{pmatrix}
|1\rangle \\
|2\rangle \\
|3\rangle \\
|4\rangle \\
|5\rangle \\
|6\rangle \\
|7\rangle \\
\end{pmatrix} = R
\begin{pmatrix}
\delta_1^\uparrow \\
\delta_1^\downarrow \\
\psi_3^P \downarrow \\
\delta_2^\downarrow \\
\delta_2^\uparrow \\
\delta_3^\downarrow \\
\delta_3^\uparrow \\
\end{pmatrix},
\]

that is, we include also the spin-up counterpart \(|7\rangle := \delta_3^\uparrow\) of orbital \(|6\rangle\). In principle we have

\[35 = \binom{7}{3}\] Slater determinants, of which eighteen have the total \(S_z\) component equal to \(\downarrow\) and fifteen are spin-adapted: the eight ones of the rank-six approximation \(b\) plus

\[ [267], [367], [567], [136] - [237], [346] - [357], [257] - [156], [257] - [246]. \]

There are four Klyachko inequalities for Li in a rank-seven configuration:

\[
\begin{align*}
\lambda_1 + \lambda_2 + \lambda_4 + \lambda_7 &\leq 2; & \lambda_1 + \lambda_2 + \lambda_5 + \lambda_6 &\leq 2; \\
\lambda_2 + \lambda_3 + \lambda_4 + \lambda_5 &\leq 2; & \lambda_1 + \lambda_3 + \lambda_4 + \lambda_6 &\leq 2.
\end{align*}
\]

In our calculations we find

\[
\begin{align*}
0 \leq D_1^7 & = 2 - (\lambda_1 + \lambda_2 + \lambda_4 + \lambda_7) = 0, \\
0 \leq D_2^7 & = 2 - (\lambda_1 + \lambda_2 + \lambda_5 + \lambda_6) = 1.3045 \times 10^{-5}, \\
0 \leq D_3^7 & = 2 - (\lambda_2 + \lambda_3 + \lambda_4 + \lambda_5) = 7.7411 \times 10^{-5}, \\
0 \leq D_4^7 & = 2 - (\lambda_1 + \lambda_3 + \lambda_4 + \lambda_6) = 8.0025 \times 10^{-5}.
\end{align*}
\]
There is a number of interesting issues on the structure of the constraints, which now shall be briefly discussed.

- The pinned system can be factorized,
  \[ \wedge^3 \mathcal{H}_7 \rightarrow \mathcal{H}_3 \otimes \wedge^2 \mathcal{H}_4. \]
  That is, the one-body matrix can be split into a direct sum of two matrices,
  \[ \rho_1 = \rho_1^\uparrow \oplus \rho_1^\downarrow. \]
  The first one is a 3 × 3 square matrix whose trace is equal to 1 and that is associated with the electron with spin pointing \( \uparrow \), while the second matrix is a 4 × 4 square matrix whose trace is equal to 2 and is associated with the two electrons with spin pointing \( \downarrow \). With the numbering already dictated by the occupancies, its entries read
  \[
  \rho_1^\uparrow(1, 1) = |c_{123}|^2 + |c_{124}|^2 + |c_{126}|^2 + |c_{235}|^2 + |c_{237}|^2 + |c_{245}|^2 + |c_{267}|^2 + |c_{268}47|^2 + |c_{256}|^2 + |c_{267}|^2
  \]
  \[
  \rho_1^\uparrow(1, 2) = c_{124}c_{134}^* + c_{126}c_{136}^* + c_{245}c_{345}^* + c_{256}c_{356}^* + c_{267}c_{367}^*
  \]
  \[
  \rho_1^\uparrow(1, 3) = -c_{123}c_{134}^* + c_{126}c_{146}^* - c_{235}c_{345}^* - c_{237}c_{347}^* + c_{256}c_{456}^* + c_{267}c_{467}^*
  \]
  \[
  \rho_1^\uparrow(1, 4) = -c_{123}c_{136}^* - c_{124}c_{146}^* + c_{235}c_{356}^* - c_{237}c_{367}^* + c_{245}c_{456}^* - c_{247}c_{467}^*
  \]
  \[
  \rho_1^\uparrow(2, 2) = |c_{123}|^2 + |c_{134}|^2 + |c_{136}|^2 + |c_{235}|^2 + |c_{237}|^2 + |c_{245}|^2 + |c_{247}|^2 + |c_{345}|^2 + |c_{347}|^2 + |c_{356}|^2 + |c_{367}|^2
  \]
  \[
  \rho_1^\uparrow(2, 3) = c_{123}c_{124}^* + c_{136}c_{146}^* + c_{235}c_{245}^* + c_{237}c_{247}^* - c_{356}c_{456}^* + c_{367}c_{467}^*
  \]
  \[
  \rho_1^\uparrow(2, 4) = c_{123}c_{126}^* - c_{134}c_{146}^* - c_{235}c_{256}^* + c_{237}c_{267}^* + c_{345}c_{456}^* - c_{347}c_{467}^*
  \]
  \[
  \rho_1^\uparrow(3, 3) = |c_{124}|^2 + |c_{134}|^2 + |c_{146}|^2 + |c_{245}|^2 + |c_{247}|^2 + |c_{345}|^2 + |c_{347}|^2 + |c_{456}|^2 + |c_{467}|^2
  \]
  \[
  \rho_1^\uparrow(3, 4) = c_{124}c_{126}^* + c_{134}c_{136}^* - c_{245}c_{256}^* + c_{247}c_{267}^* - c_{345}c_{356}^* + c_{347}c_{367}^*
  \]
  \[
  \rho_1^\uparrow(4, 4) = |c_{126}|^2 + |c_{136}|^2 + |c_{146}|^2 + |c_{256}|^2 + |c_{257}|^2 + |c_{356}|^2 + |c_{357}|^2 + |c_{456}|^2 + |c_{457}|^2.
  \]

• For the first time we see the appearance of two scales of quasi-pinning.

• If the second constraint were saturated, the selection rule fixes the number of Slater determinants in the decomposition of the wave function to be nine,
  \[ [\alpha_1\alpha_2\alpha_3], [\alpha_1\alpha_4\alpha_5], [\alpha_1\alpha_4\alpha_6], [\alpha_1\alpha_5\alpha_7], [\alpha_1\alpha_6\alpha_7], [\alpha_2\alpha_4\alpha_5], [\alpha_2\alpha_4\alpha_6], [\alpha_2\alpha_5\alpha_7], [\alpha_2\alpha_6\alpha_7]. \]
• As for the case of $\Lambda^3 \mathcal{H}_6$, the loss of information when projecting the total wave function onto this nine-dimensional subspace of twice pinned states can be estimated. In appendix B we give a proof of the following theorem: let a wave function $|\Phi\rangle \in \Lambda^3 \mathcal{H}_7$ with natural orbitals $|\alpha_i\rangle_{i=1}^7$, occupation numbers $\{\lambda_i\}_{i=1}^7$, saturating the first restriction. Moreover, let $P_7$ be the projection operator onto the subspace spanned by the Slater determinants above. Then, the upper and lower bounds of this projection are given by

$$1 - \frac{1 + 9\xi}{1 - 11\xi} D_7^2 \leq \|P_7\Phi\|_2^2 \leq 1 - \frac{1}{2} D_7^2 \quad \text{provided that} \quad \xi < \frac{1}{11}. $$

Within our calculations, $1 - \frac{1 + 9\xi}{1 - 11\xi} D_7^2 = 1 - 1.3852 \times 10^{-5} = 99.9986\%$.

• If, in addition, the third or the fourth constraint becomes saturated, the selection rules decreases the number of allowed determinants to just 4. Saturating both simultaneously reduces the case to the saturated rank-six wavefunction.

We omit the expressions of the two-body and two-hole matrices, which can be easily calculated. It should, however, be added that the tensor character under rotations of the reduced matrices for a three-electron system is quite different from the one for a two-electron system; in particular the relative weight in the lithium isoelectronic series of the six components identified in [15, Sect. 6A] or [16] deserves some further study.

5.2 Quasi-pinning displayed in the rank-eight approximation

We can obtain rank eight by adding a new orbital $|8\rangle := \delta_{4\downarrow}$, giving now $\binom{3}{1} \binom{2}{1} = 30$ Slater determinants with the correct $z$-component of the spin. Among them, 21 are spin-adapted, i.e., the fifteen ones of the rank-seven approximation, plus

$[128], [458], [678], [148] - [258], [168] - [278], [568] - [478]$. 

The number of Klyachko inequalities grows notably with the rank. We find 31 inequalities in [1]. Of those, 28 constraints are displayed in our Table 4.

In the table, we have included the values of the inequalities that result from our calculation, and in order to analyze those further, we have plotted them both in a linear and in a logarithmic scale in Fig. 3. The presence of several scales is clearly seen. Moreover, conditions involving the eighth occupation number are clearly weaker than the previous ones. The main point, which both confirms and extends the findings for the toy model in [5], is the robustness of quasipinning. In particular, the quantity $D_8^1$, found to be exactly zero in the previous rank, remains in a strongly pinned regime.

Finally, one can examine the effect of the saturation conditions and the resulting dramatic reduction of the number of Slater determinants, as well as the simplification of the corresponding two-body matrix. This remarkable evolution is visualized in Fig. 4.
Table 4: Klyachko inequalities for a system \( \wedge^3 \mathcal{H}_8 \) and some numerical values for Li.
6 Conclusion

By means of numerical calculations, we have explored the nature of the quasi-pinning in real three-electron atoms. In the space $\wedge^3\mathcal{H}_6$, for restricted spin-orbitals we find that the Klyachko constraint is saturated. For unrestricted configurations, quasi-pinning is bounded by the lowest occupation number $\lambda_6$. In approximations of larger rank, the Klyachko constraints split into well differentiated groups of different levels of saturation. In other words, for a real system we find results compatible with those found previously for the model system [5]. A simple geometric probability argument also suggests stability of quasi-pinning. Moreover, whenever $3 - \lambda_1 - \lambda_2 - \lambda_3$ is not far from zero, projecting the complete wave function of the CI picture into the set of pinned states appears to result in negligible loss of information. Thus, the Klyachko-guided addition of a few Slater determinants to Hartree–Fock type states

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Figure 3: Plot of the inequalities of Table 4 in (a) values of $10^{-3}$ and (b) a logarithmic scale.

Figure 4: (Color online) Evolution of the dimension of the space of Slater determinants as a function of Klyachko’s saturations for rank six, seven and eight.
becomes a low-cost approach to accurate atomic wave functions.

In addition, through our work we have verified some recent results of quantum information theory for three-electron systems. In particular, we find non-trivial, but fairly low, quantum entanglement in ground states.

Even if the present study is a step towards a general description of real systems, the system of our study is special in a couple of aspects. The Hartree–Fock approximation is a good starting point for the Li-like atoms, and the system has a high spherical symmetry. In future work we hope to address cases where the occupation numbers will not lie so close to 0 or 1, and/or the symmetry is reduced. We will thereby be able to explore whether the conclusions we have drawn in the present study hold more generally in chemistry.

A On the nature of the Klyachko restrictions

Here, we shall not give proofs of the Klyachko constraints but just discuss some few aspects of relevance to the present work. It is useful to consider the skew Cauchy formula,

$$\bigwedge^N (\mathcal{H}_s \otimes \mathcal{H}_{\text{orb}}) = \sum_{|\kappa|=N} \mathcal{H}_s^\kappa \otimes \mathcal{H}_{\text{orb}}^{\bar{\kappa}}. \quad (14)$$

Here, $\kappa$ denotes the representation corresponding to the partition or Young tableau $\kappa$, and $\bar{\kappa}$ is the dual partition.

In the present work we have exclusively the case $\dim \mathcal{H}_s = 2$ and $N = 3$, which makes everything relatively simple. The three-electron state space splits into spin-orbital sectors, which one needs to specify in order to check quasi-pinning, as well as to gauge entanglement. $\mathcal{H}_s$ corresponds to a spin-$\frac{3}{2}$ particle. Therefore, on the left hand side we may have only representations of $SU(2)$, i.e., either $j = \frac{1}{2}$ or $j = \frac{3}{2}$ for three particles. Since there are no skewsymmetric combinations of three spins-$\frac{1}{2}$, the partition $(1, 1, 1)$ on the right hand side plays no role; consequently, only tableaux with up to two columns may appear on the left hand side.

Consider for instance the first non-trivial case $\bigwedge^3(\mathcal{H}_2 \otimes \mathcal{H}_3)$ in the configuration $6^a$ of Section 4. There are 20 configurations in all. Clearly there is one with three spin down and one with three spin up, belonging to the representation with $j = \frac{3}{2}$. Of the eighteen remaining states, nine have one spin down in total, and nine have spin up. But only eight of each belong to the $j = \frac{1}{2}$ representation; the other two belong to $j = \frac{3}{2}$, whereby the spatial orbitals enter in the unique completely skewsymmetric combination. This takes care of “spin contamination”. Accordingly,

$$\bigwedge^3(\mathcal{H}_2 \otimes \mathcal{H}_3_{\text{orb}}) = \downarrow H_2^{\otimes 3} \oplus \uparrow H_2^{\otimes 3} + H_2^{3/2} \otimes \bigwedge^3 H_{3_{\text{orb}}}. \quad (14)$$

From these simple observations to the generalized Pauli constraints there is still a long haul, demanding generous dollops of Kirillov’s theory of orbits of the coadjoint action for compact groups \footnote{\textsuperscript{[1]}}; the surprising outcome is that only linear inequalities are found.

Of course, not all of our basis sets conform to the left hand side of (14). This causes no problem, however, since any basis set can be considered a special case of a larger one with
the “right” structure, with some holes. Important is it that the Klyachko restrictions are consistent, so lower-rank ones can be derived from higher-rank ones. Recall for instance our example $\Lambda^3 \mathcal{H}_7$, and the four corresponding relations:

\[
\begin{align*}
\lambda_1 + \lambda_2 + \lambda_4 + \lambda_7 & \leq 2; \\
\lambda_2 + \lambda_3 + \lambda_4 + \lambda_5 & \leq 2; \\
\lambda_1 + \lambda_3 + \lambda_4 + \lambda_6 & \leq 2.
\end{align*}
\]

At first, the original Pauli principle $\lambda_1 \leq 1$ is perhaps not entirely obvious here; it follows from summing the second and the fourth. Also, let us consider the case $\lambda_7 = 0$. Then summing the second and the third we obtain $\lambda_2 + \lambda_5 \leq 1$; the second and fourth yield $\lambda_3 + \lambda_4 \leq 1$, and so on: we plainly recover the Borland–Dennis relations for $\Lambda^3 \mathcal{H}_6$. The reader will have no difficulty in retrieving all the lower-rank relations from the ones on $\Lambda^3 \mathcal{H}_8$.

\section*{B Bounds for the rank-seven approximation}

\textbf{Theorem 1.} Let $|\Phi\rangle \in \Lambda^3 \mathcal{H}_7$ be a wave function with natural orbitals $\{ |\alpha_i\rangle \}_{i=1}^7$ and occupation numbers $\{ \lambda_i \}_{i=1}^7$ arranged in decreasing order. Let $P_L$ be the projection operator onto the subspace spanned by the Slater determinants

\[
[\alpha_1 \alpha_2 \alpha_3], [\alpha_1 \alpha_4 \alpha_5], [\alpha_1 \alpha_4 \alpha_6], [\alpha_2 \alpha_5 \alpha_7], [\alpha_2 \alpha_4 \alpha_5], [\alpha_2 \alpha_5 \alpha_7], [\alpha_2 \alpha_6 \alpha_7].
\]

Upper and lower bounds of this projection are given by

\[
1 - \frac{1 + \frac{9c}{11} \xi}{1 - 11 \xi} D_L^2 \leq \| P_L |\Phi\rangle \|^2 \leq 1 - \frac{1}{2} D_L^2, \quad \text{where } \xi := 3 - \lambda_1 - \lambda_2 - \lambda_3 < \frac{1}{11}.
\]

\textbf{Proof.} Let $J_1 = \{ 3, 5, 6 \}$ and $J_2 = \{ 1, 2, 4, 7 \}$. A general wave function in $\Lambda^3 \mathcal{H}_7$ is given by

\[
|\Phi\rangle = \sum_{k \in J_1} \sum_{i,j \in J_2} c_{ijk} |\alpha_i \alpha_j \alpha_k\rangle \quad \text{and consequently } \lambda_m = \sum_{k \in J_1} \sum_{i,j \in J_2} m \in \{ i,j,k \} |c_{ijk}|^2.
\]

Therefore,

\[
\begin{align*}
\lambda_1 &= |c_{123}|^2 + |c_{125}|^2 + |c_{126}|^2 + |c_{134}|^2 + |c_{145}|^2 + |c_{146}|^2 + |c_{137}|^2 + |c_{157}|^2 + |c_{167}|^2; \\
\lambda_2 &= |c_{123}|^2 + |c_{125}|^2 + |c_{126}|^2 + |c_{234}|^2 + |c_{245}|^2 + |c_{246}|^2 + |c_{237}|^2 + |c_{257}|^2 + |c_{267}|^2; \\
\lambda_5 &= |c_{125}|^2 + |c_{145}|^2 + |c_{157}|^2 + |c_{245}|^2 + |c_{257}|^2 + |c_{457}|^2; \\
\lambda_6 &= |c_{126}|^2 + |c_{146}|^2 + |c_{167}|^2 + |c_{246}|^2 + |c_{267}|^2 + |c_{467}|^2.
\end{align*}
\]

A simple computation gives

\[
\lambda_1 + \lambda_2 + \lambda_5 + \lambda_6 = 2|c_{123}|^2 + 2|c_{125}|^2 + 2|c_{126}|^2 + 2|c_{134}|^2 + 2|c_{145}|^2 + 2|c_{146}|^2 + 2|c_{137}|^2 + 2|c_{157}|^2 + 2|c_{167}|^2 + 2|c_{234}|^2 + 2|c_{245}|^2 + 2|c_{246}|^2 + 2|c_{237}|^2 + 2|c_{257}|^2 + 2|c_{267}|^2 + 2|c_{457}|^2 + 2|c_{467}|^2. \quad \text{And trivially } D_L^2 = 2 - (\lambda_1 + \lambda_2 + \lambda_5 + \lambda_6) = L + S - |c_{125}|^2 - |c_{126}|^2;
\]

20
where \( S := 2|c_{347}|^2 + |c_{457}|^2 + |c_{467}|^2 \) and \( L := |c_{134}|^2 + |c_{137}|^2 + |c_{234}|^2 + |c_{237}|^2 \). Thus, for the projection onto the aforementioned subspace we have
\[
\| P_7 \Phi \|_2^2 = |c_{123}|^2 + |c_{145}|^2 + |c_{146}|^2 + |c_{157}|^2 + |c_{167}|^2 + |c_{245}|^2 + |c_{246}|^2 + |c_{257}|^2 + |c_{267}|^2 \\
\leq 1 - \| (L + 2c_{437})^2 + |c_{125}|^2 + |c_{457}|^2 + |c_{467}|^2 \| \leq 1 - \frac{1}{2}(L + 2c_{437})^2 - |c_{125}|^2 + |c_{457}|^2 - |c_{126}|^2 + |c_{467}|^2 = 1 - \frac{1}{2}D_7^2,
\]
which is the upper bound of \([15]\).

To establish the lower bound, note that in the basis of natural orbitals we know that
\[
\langle \alpha_6 | \rho_1 | \alpha_3 \rangle = c_{123}c_{126} - c_{134}c_{146} + c_{137}c_{167} - c_{234}c_{246} + c_{237}c_{267} - c_{347}c_{467} = 0 \\
\langle \alpha_5 | \rho_1 | \alpha_3 \rangle = c_{123}c_{125} - c_{134}c_{145} + c_{137}c_{157} + c_{234}c_{245} + c_{237}c_{257} - c_{347}c_{457} = 0.
\]
Let \( \epsilon := c_{123} \), the amplitude of the Hartree–Fock determinant. Using the Cauchy inequality
\((A + B + C + D + E)^2 \leq 5(A^2 + B^2 + C^2 + D^2 + E^2)\) as well as \(|c_{abc}|^2 \leq 1 - |\epsilon|^2\) whenever \(abc \neq 123\), we obtain:
\[
|c_{126}|^2 \leq \frac{5}{|\epsilon|^2} \left[ |c_{134}|^2 |c_{146}|^2 + |c_{137}|^2 |c_{167}|^2 + |c_{234}|^2 |c_{246}|^2 + |c_{237}|^2 |c_{267}|^2 + |c_{347}|^2 |c_{467}|^2 \right] \\
\leq \frac{5(1 - |\epsilon|^2)}{|\epsilon|^2} \left[ L + \frac{1}{2}(|c_{347}|^2 + |c_{467}|^2) \right] \quad \text{and}
\]
\[
|c_{125}|^2 \leq \frac{5}{|\epsilon|^2} \left[ |c_{134}|^2 |c_{145}|^2 + |c_{137}|^2 |c_{157}|^2 + |c_{234}|^2 |c_{245}|^2 + |c_{237}|^2 |c_{257}|^2 + |c_{347}|^2 |c_{457}|^2 \right] \\
\leq \frac{5(1 - |\epsilon|^2)}{|\epsilon|^2} \left[ L + \frac{1}{2}(|c_{347}|^2 + |c_{457}|^2) \right].
\]

Let us set, for some \( r, u \geq 0, \)
\[
L + |c_{347}|^2 + |c_{125}|^2 + |c_{457}|^2 + |c_{126}|^2 + |c_{467}|^2 \\
\leq L + (1 + u)S + (1 - r)(|c_{125}|^2 + |c_{126}|^2) + r(|c_{125}|^2 + |c_{126}|^2) \\
\leq L + (1 + u)S + (1 - r)(|c_{125}|^2 + |c_{126}|^2) + \frac{5r(1 - |\epsilon|^2)}{|\epsilon|^2} \left[ 2L + \frac{1}{2}S \right] \\
= \left[ 1 + \frac{10r(1 - |\epsilon|^2)}{|\epsilon|^2} \right] L + (1 - r)(|c_{125}|^2 + |c_{126}|^2) + \left[ (1 + u) + \frac{5r(1 - |\epsilon|^2)}{2|\epsilon|^2} \right] S.
\]

By choosing
\[
r = \frac{2|\epsilon|^2}{11|\epsilon|^2 - 10} \quad \text{and} \quad u = \frac{15(1 - |\epsilon|^2)}{11|\epsilon|^2 - 10} \quad \text{with} \quad |\epsilon|^2 > 10/11,
\]
we obtain that \( L + |c_{347}|^2 + |c_{125}|^2 + |c_{457}|^2 + |c_{126}|^2 + |c_{467}|^2 \leq (r - 1)D_7^2 \). It is now clear that
\[
\| P_7 \Phi \|_2^2 = 1 - (L + |c_{347}|^2 + |c_{125}|^2 + |c_{457}|^2 + |c_{126}|^2 + |c_{467}|^2) \\
\geq 1 - (r - 1)D_7^2 = 1 - \frac{1 + 9(1 - |\epsilon|^2)}{1 - 11(1 - |\epsilon|^2)} D_7^2 \geq 1 - \frac{1 + 9\xi}{1 - 11\xi} D_7^2,
\]
where in the last inequality we have used \( 1 - |\epsilon|^2 \leq \xi = 3 - \lambda_1 - \lambda_2 - \lambda_3 \), which is Lemma 3 in [14]. □
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