Why doubly excited determinants govern configuration interaction calculations of electron correlations

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Computational evidence shows that, when using natural orbitals to study (dynamical and non-dynamical) electron correlation, determinants with an odd number of excitations play a negligible role. Instead, doubly excited determinants rule the rostrum in this kind of configuration interaction calculations. We explain mathematically why it must be so.

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Introduction. Postulated by Pauli to explain the electronic structure of atoms and molecules, the exclusion principle states that each quantum state cannot be occupied by more than one electron. As Dirac pointed out, this principle emerges from antisymmetry imposed on the wave function \(|\Psi\rangle\). The exclusion principle can be stated by saying that the fermionic natural occupation numbers (NON), which are the eigenvalues of the one-body reduced density matrix (arranged in decreasing order \(n_i \geq n_{i+1}\)) must fulfill the constraint \(n_1 \leq 1\). In the sixties Coleman [2] proved that this inequality is necessary and sufficient for a one-body density matrix to come from the reduction of an ensemble \(N\)-body density matrix, provided that \(\sum_i n_i = N\).

In the Configuration Interaction (CI) picture, the antisymmetry of the wave function is ensured by writing it as a linear combination of all possible configurations,

\[
|\Psi\rangle = \sum c_i |\ell\rangle,
\]

where \(|\ell\rangle\) denotes a Slater determinant, in a given spin-orbital basis, the eigenvectors of the one-body reduced orbital basis. In this paper we use the basis of natural orbitals (NO), the eigenvectors of the one-body reduced density matrix.

In a seminal article, Borland and Dennis observed generalizations of Pauli conditions (GPC) for the rank-six approximation of a pure state three-electron system [3]. The NON satisfy the constraints:

\[
n_j + n_{-j} \leq 1, \text{ where } j \in \{1, 2, 3\};
\]

\[
\text{and } n_4 \leq n_5 + n_6.
\]

Then the question of possible GPC lay dormant for many years. Only a few years ago, a standardized approach to them by profound group-representation methods was devised by Klyachko [4]. This reveals a rich substructure in fermion systems, recently exploited in theoretical chemistry, entanglement theory and ferromagnetism [5, 11].

The Klyachko algorithm produces sets of linear inequalities for the \(m\) NON of the pure state \(|\Psi\rangle\) in \(\mathbb{R}^m\) of \(n\) electrons arranged in \(m\) spin orbitals, similar to those of [2]. Namely,

\[
D_{n,m}^\mu (\mathbf{n}) = \kappa_0^\mu + \kappa_1^\mu n_1 + \cdots + \kappa_n^\mu n_m \geq 0,
\]

with \(\mathbf{n} = (n_1, \ldots, n_m)\) and integer coefficients \(\kappa_i^\mu\). For instance, the generalization \(n_i + n_{2k+1-j} \leq 1\) of the first equations in [2] holds in any even rank \(m = 2k\). The inequalities define a convex polytope of allowed states in \(\mathbb{R}^m\).

By definition, a pinned system saturates completely some of the GPC. That is, for some \(\mu\) indexing the corresponding equalities [3], the condition \(D_{n,m}^\mu (\mathbf{n}) = 0\) holds, and then the system lies on one of the faces of the polytope. For such there is a selection rule given in [12], involving the terms in the decomposition [11]. To wit, define the operator

\[
\mathbf{D}_{n,m}^\mu = \kappa_0^\mu \mathbf{1} + \kappa_1^\mu \mathbf{a}_1 \mathbf{a}_1 + \cdots + \kappa_n^\mu \mathbf{a}_m \mathbf{a}_m,
\]

where \(\mathbf{a}_i\) and \(\mathbf{a}_i^\dagger\) are the creation and annihilation fermionic operators for the state \(i\). Given a system satisfying \(\mathbf{D}_{n,m}^\mu (\mathbf{n}) = 0\), each Slater determinant in the expansion [11] is an eigenfunction of \(\mathbf{D}_{n,m}^\mu\) with eigenvalue zero (say, effective configurations). In other words:

\[
\text{if } \mathbf{D}_{n,m}^\mu |\ell\rangle \neq 0, \text{ then } c_i = 0,
\]

and therefore \(\mathbf{D}_{n,m}^\mu |\Psi\rangle = 0\).

This extremely plausible statement, valid for nondegenerate NON, actually needs proof, which is forthcoming [13]. It enables the wave function to be described by Ansätze that drastically reduce the number of Slater determinants in the CI expansion. Numerical investigations for real atoms and molecules [6, 7] have already confirmed that pinning often takes place. Even more mysteriously, there is a remarkable prevalence of quasipinning (almost saturation of the Klyachko inequalities) —and not only for ground states.
Now, recent evidence shows that, when using the basis of NO (as distinct from Hartree–Fock molecular orbitals, say) to study bond weakening and breaking, doubly excited determinants are dramatically enhanced with respect to singly and triply excited ones [13]. In turn, this motivates the introduction of a (quite successful) “extended Löwdin–Shull” 1-RDM functionals, sharing some of the simplicity of the original Löwdin–Shull formula for the wave function of a two-electron system [15]. In this paper we argue that such an outstanding phenomenon stems from Klyachko pinning, which eliminates first and foremost oddly-excited configurations.

Rank-six three-electron systems. For simplicity, we consider three-electron systems, mostly described with the help of restricted spin orbital bases. Besides the lithium isoelectronic series, already thoroughly examined in [6, 7], we base ourselves on data for perturbed lithium with broken spherical symmetry, and for the dimer ion He$_2^+$, for several ranks [10].

Before proving our main result, it is instructive to understand it first in the context of the Borland–Dennis paper we argue that such an outstanding phenomenon stems from Klyachko pinning, which eliminates first and foremost oddly-excited configurations.

Indeed: the operator $\sum_{i=1}^6 n_i = 3$, the Klyachko inequalities

$$n_1 + n_6 \leq 1, \quad n_2 + n_5 \leq 1, \quad n_3 + n_4 \leq 1$$

are in fact pinned. This selects a combination of eight states, living in $\mathcal{H}_2^3$. We may denote the three pairs of NO by $\{\alpha_1, \alpha_6\}$, $\{\alpha_2, \alpha_3\}$, $\{\alpha_3, \alpha_4\}$. Note the following: if we decide that the spin of the ground state is $\uparrow$ (say), then with our basis we construct nine corresponding eigenfunctions of $S_z$; however, one of these configurations belongs in the representation with $j = 3/2$. So we have automatically obtained the correct counting of states. There are three singly-excited determinants and a triply-excited one.

Furthermore, for the chosen basis of restricted spin orbitals, we are able to prove [10] that pinning of the last constraint $n_4 = n_5 + n_6$ or $1 + n_3 = n_1 + n_2$ in (2) always applies. With that pinning, the three single excitations, the triple excitation and one double excitation disappear, so one needs only three configurations, instead of eight. Indeed: the operator $1 - a_1^\dagger a_3 - a_2^\dagger a_5 + a_4^\dagger a_6$ does not “kill” singly-excited configurations, so these cannot enter the wave function. It does not kill the triple configuration either; nor does it kill the doubly-excited configuration $|\alpha_3\alpha_5\alpha_6\rangle$. Thus only the configurations $|\alpha_1\alpha_4\alpha_5\rangle$ and $|\alpha_2\alpha_4\alpha_6\rangle$, besides $|\alpha_1\alpha_2\alpha_3\rangle$, are available.

In conclusion, one rather efficiently has, for any state constructed according to our specification:

$$|\Psi\rangle_{3.6} = a |\alpha_1\alpha_2\alpha_3\rangle + b |\alpha_1\alpha_4\alpha_5\rangle + c |\alpha_2\alpha_4\alpha_6\rangle,$$

with

$$n_1 = |a|^2 + |b|^2 \geq n_2 = |a|^2 + |c|^2, \quad n_5 = |b|^2, \n_3 = |a|^2 \geq n_4 = |b|^2 + |c|^2, \quad n_6 = |c|^2,$$ (5)

for the NON. (In the simpler, somewhat degenerate case $m = 5$, two single excitations and, as before, one double excitation are ineffective.)

Rank seven. For higher ranks, we look at the theoretical and computational situations in parallel. For $m = 7$ the Klyachko setup of inequalities is still mercifully small. To wit, there are only four constraints in $\wedge^3\mathcal{H}_7$:

$$D_{3.7}^1 := 2 - n_1 - n_2 - n_4 - n_7 \geq 0,$$

$$D_{3.7}^2 := 2 - n_1 - n_2 - n_5 - n_6 \geq 0,$$

$$D_{3.7}^3 := 2 - n_1 - n_3 - n_4 - n_5 \geq 0,$$

$$D_{3.7}^4 := 2 - n_2 - n_3 - n_4 - n_6 \geq 0.$$

Notice that the Klyachko restrictions are consistent, in that lower-rank ones can be derived from higher-rank ones. For instance, if $n_7 = 0$ above, then summing the second and third we obtain $n_1 + n_6 \leq 1$; the second and fourth yield $n_2 + n_5 \leq 1$, and so on: we recover all the Borland–Dennis relations for $\wedge^3\mathcal{H}_6$. To be sure, the original Pauli principle $n_1 \leq 1$ follows from them, too.

Numerical investigations for the lithium series have shown the system to be always pinned to the first constraint [6, 7]. Moreover, the second constraint happens to be nearly saturated. Remarkably, for He$_2^+$ in its ground state the situation appears to be reversed: the second constraint is saturated exactly, while the first one is saturated to a good approximation [10].

Table 1 contains the NON for rank-six up to rank-eight approximations for the dimer ion He$_2^+$, as computed using a STO-6G basis set [10]. For rank-seven, the second GPC is completely saturated, while the first GPC belongs to a highly saturated regime:

$$D_{3.7}^3 = 2.41 \times 10^{-6}.$$ 

The other two constraints belong to a different scale of quasipinning: we had already detected these “successive scales of quasipinning” in [6]. In fact,

$$D_{3.7}^1 = 3.18 \times 10^{-4} \quad \text{and} \quad D_{3.7}^4 = 8.24 \times 10^{-4}.$$ 

It seems fair to conclude that there is a tendency to strong quasipinning of the two first GPC in this approximation. If both were saturated, then $1 + n_3 = n_1 + n_2$ would follow. Indeed, we would have:

$$2 = n_1 + n_2 + n_4 + n_7 \quad \text{and} \quad 2 = n_1 + n_2 + n_5 + n_6.$$ 

| Rank | $n_1$ | $n_2$ | $n_3$ | $n_4(-3)$ | $n_5(-3)$ | $n_6(-4)$ | $n_7(-4)$ | $n_8(-5)$ |
|------|-------|-------|-------|-----------|-----------|-----------|-----------|-----------|
| 6    | 0.9993 | 0.9938 | 0.9932 | 6.75       | 6.14      | –         | –         | –         |
| 7    | 0.9989 | 0.9938 | 0.9928 | 6.56       | 6.38      | 7.6       | 5.7       | –         |
| 8    | 0.9990 | 0.9953 | 0.9943 | 5.06       | 5.02      | 5.9       | 5.2       | 2.1       |

Table 1. NON corresponding to rank-six up to rank-eight approximations for He$_2^+$ at its equilibrium geometry.
Summing these two equalities, we see that
\[ 4 = 2n_1 + 2n_2 + n_4 + n_5 + n_6 + n_7 = 3 - n_3 + n_1 + n_2, \]
where we have used \( \sum n_i = 3 \). This means again that all singly excited and triply excited determinants are suppressed, and the number of effective configurations, all of which are doubly excited, drops sharply.

A telling example of further disappearance of excitations in the context of \( m = 7 \) is discussed by Klyachko in [12]. It happens in the first excited state of Be with spin data \((S, S_z) = (1,1)\), whose first occupation number is frozen to one, so we may regard it as a three-electron system. Numerical calculations for this state suggest further pinning. Imposing saturation of the third remaining constraint, four configurations are left:
\[
\begin{align*}
n_1 &= |a|^2 + |b|^2 + |d|^2 \geq n_2 = |c|^2 + |d|^2, \\
n_3 &= |a|^2 \geq n_4 = |b|^2 + |c|^2, \\
n_5 &= |b|^2 \geq n_6 = |c|^2 + |d|^2, \\
n_7 &= |d|^2,
\end{align*}
\]
with \(|\Psi\rangle_{3,7}\) being
\[ a |\alpha_1\alpha_2\alpha_3\rangle + b |\alpha_1\alpha_4\alpha_5\rangle + c |\alpha_2\alpha_4\alpha_6\rangle + d |\alpha_1\alpha_6\alpha_7\rangle. \]
The case \(D_{1,7} |\Psi\rangle = 0\), when both \(D_{1,7}\) and \(D_{2,7}\) are saturated, would be similar, with \(|\alpha_2\alpha_5\alpha_7\rangle\) replacing \(|\alpha_1\alpha_6\alpha_7\rangle\). Formulas (5) come smoothly from (6) when \(d = 0\).

This is perhaps the place to invoke evidence from the toy model of spinless “fermions” on the line, subjected to a harmonic potential and a harmonic interaction, studied in [3]. The strength of the latter interaction can be described by a suitable parameter \(\delta\), whose vanishing implies that the ground state is a single determinant with trivial NON. Perturbatively in the interaction, it is found for \(N = 3\) that corrections to the NON are of order \(\delta^4\). However, the relation \(1 + n_3 = n_1 + n_2\) is violated only at order \(\delta^8\). So there also quasipinning is patent; on the other hand, due to the existence of spin, real electronic systems are more rigidly pinned.

**Rank eight.** Let us go now to \(m = 8\). The dimension of the Hilbert space is \(\binom{8}{3}\). Putting aside again the issue of spin contamination, the sector in which we are interested contains 24 configurations, corresponding to \(\wedge^2 H_4 \otimes H_4\), of which clearly 7 are singly excited and 3 are triply excited. The condition \(1 + n_3 \geq n_1 + n_2\) still holds.

Table II contains the numerical values of the first ten \((31)\) GPC for the rank-eight approximation to the ground state of the molecule \(\text{He}_2^+\) and lithium [6] [10]. The constraint \(D_{2,8} \geq 0\) appears to be saturated exactly for the diatomic ion; and the constraints
\[
\begin{align*}
D_{1,8}^1 &\geq 0, & D_{3,8}^5 &= 1 - n_1 - n_2 + n_3 \geq 0,
\end{align*}
\]
nearly so. For the lithium isoelectronic series, we have chosen to show data obtained by working with unrestricted spin orbitals. Restricted ones actually yield better values for the energy and exhibit pinning. The point is that even by working with unrestricted ones, the same constraints are also very nearly saturated.

The “unreasonable effectiveness” of the single quasi-pinning \(1 + n_3 \approx n_1 + n_2\) is here again enough to suppress the odd excitations, obtaining a reduction to 13 (the strongly occupied one plus 12 doubly excited) configurations. The operator
\[
D_{3,8}^5 = 1 - a_i^\dagger a_1 - a_j^\dagger a_2 + a_k^\dagger a_3
\]
does kill 12 double excitations:
\[
|\alpha_1\alpha_2\alpha_3\rangle, |\alpha_1\alpha_4\alpha_5\rangle, |\alpha_1\alpha_4\alpha_6\rangle, |\alpha_1\alpha_7\alpha_3\rangle, |\alpha_1\sigma_1\alpha_6\rangle, |\alpha_1\sigma_2\alpha_3\rangle, |\alpha_2\alpha_4\alpha_5\rangle, |\alpha_2\alpha_4\alpha_6\rangle, |\alpha_2\alpha_7\alpha_3\rangle, |\alpha_2\sigma_1\alpha_6\rangle, |\alpha_2\sigma_2\alpha_3\rangle, |\alpha_2\sigma_7\alpha_3\rangle,
\]
which are the survivors. The double excitation \(|\alpha_3\alpha_4\alpha_7\rangle\) drops out, as well. Further (quasi)pinning selects out other double excitations; we refer to [10] for that.

Figure 11 exhibits the behavior of those three GPC as functions of the \(\text{He}_2^+\) bond length. Notice the sudden, intriguing crossover of two constraints at lengths smaller than that of equilibrium (namely, 2.06 au). This apparent quenching of degrees of freedom deserves further investigation.

We summarize our findings in a quite parsimonious proposition.

**The wave function of a three-fermion system, whose NON satisfy the saturated Borland-Dennis-Klyachko condition \(1 + n_3 = n_1 + n_2\), contains no odd excitations.**

**Proof.** Let us write the wave function as follows, with \(1 \leq i < j < k \leq m\) always:
\[
|\Psi\rangle = \sum_{i<j<k} c_{ijk} |\alpha_i\alpha_j\alpha_k\rangle; \quad \text{so} \quad n_a = \sum_{a \in \{i,j,k\}} |c_{ijk}|^2.
\]

| GPC | He$_2^+$ | Li |
|-----|--------|----|
| $D_{3,8}^1 = 2 - n_1 - n_2 - n_4 - n_7$ | 0.0259 | 0.0017 |
| $D_{3,8}^2 = 2 - n_1 - n_2 - n_5 - n_6$ | 0.0000 | 0.0200 |
| $D_{3,8}^3 = 2 - n_2 - n_3 - n_4 - n_5$ | 0.1793 | 0.0671 |
| $D_{3,8}^4 = 2 - n_4 - n_3 - n_5 - n_6$ | 0.9036 | 0.0894 |
| $D_{3,8}^5 = 1 - n_1 - n_2 + n_3$ | 0.0048 | 0.0200 |
| $D_{3,8}^6 = 1 - n_2 - n_5 + n_7$ | 0.1582 | 0.0854 |
| $D_{3,8}^7 = 1 - n_1 - n_6 + n_7$ | 0.8826 | 0.1078 |
| $D_{3,8}^8 = 1 - n_2 - n_4 + n_6$ | 0.1841 | 0.0671 |
| $D_{3,8}^9 = 1 - n_1 - n_4 + n_5$ | 0.9084 | 0.0894 |
| $D_{3,8}^{10} = 1 - n_3 - n_4 + n_7$ | 1.0619 | 0.1548 |
The wave function, subject to the condition $1 + n_3 = n_1 + n_2$, then reads:

$$|\Psi\rangle_{3,m} = c_{123} |\alpha_1 \alpha_2 \alpha_3 \rangle + \sum_{4 \le j < k \le m} [c_{1jk} a_j^\dagger a_k^\dagger a_3 + c_{2jk} a_j^\dagger a_2^\dagger a_3 + c_{3jk} a_j^\dagger a_3^\dagger a_3] |\alpha_1 \alpha_2 \alpha_3 \rangle.$$ 

Of course in practice we will not have $1 + n_3 = n_1 + n_2$ exactly most of the time; but all the evidence so far available points to very strong quasipinning here.

**Conclusion.** For four-electron molecules, the GPC $2 + n_4 \ge n_1 + n_2 + n_3$ holds. If it is nearly saturated, as in the case of the excited state of Be already discussed, an almost identical argument to the above shows that simply, triply and quadruply excited configurations are suppressed [10]. Many even-number electron systems fulfill the Smith identities $n_1 = n_2$, $n_3 = n_4$, . . . . Quasipinning of the last indicated GPC in this case translates simply into $n_1 \simeq 1$. The tug-of-war between energy minimization and Pauli kinematics often means that some electrons are frozen in lower shells and active spaces of smaller dimension emerge [7,8]. Then the “precipitous drop” in single excitations seen in the analysis of BH [14], with two electrons frozen, leaves little doubt that the mechanism just described is at work there. Molecules with higher number of electrons and multiple bonds constitute the next frontier, already being explored.

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