Recall, that the original Pauli exclusion principle claims that no quantum state can be occupied by more than one electron [1]. This sets a bound on expected number of electrons in any given state $\psi$:

$$\langle \psi | \rho | \psi \rangle \leq 1.$$  

(1)

Here $\rho = \sum_{ij} |\psi_i \rangle \langle \psi_j|\psi_i \rangle \langle \psi_j|$ is Dirac’s density matrix of $N$-electron system in state $\psi$. Soon after Pauli discovery, Heisenberg and Dirac [2] replaced it by skew symmetry of the multi-electron wave function

$$\Psi \in \wedge^N \mathcal{H}_r \subset \mathcal{H}^\otimes N,$$

(2)

where the wedge stands for skew symmetric tensors built on the one-electron spin-orbital space $\mathcal{H}_r$ of dimension $r$

In this Letter I first briefly review a recent solution of a longstanding problem about impact of the Dirac–Heisenberg replacement on the electron density matrix [3]. It goes far beyond the original Pauli principle and leads to numerous extended Pauli constraints independent of $\mathbb{1}$. In the rest of the paper I discuss some of their physical implications.

The problem has a long and complicated history. A difference between the two versions of Pauli principle is best seen in Heisenberg’s exchange term in electron energy. By adding this term Fock drastically improved Hartree mean field theory which initially complies the exchange energy. By adding this term Fock drastically improved Hartree mean field theory which initially complies the exchange energy. By adding this term Fock drastically improved Hartree mean field theory which initially complies the exchange energy.

A rigorous proof has been found about the same time by M.B. Ruskai, who published it only recently [6].

These (in)equations may challenge our physical intuition. They allow exactly one electron in two symmetrical natural orbitals and clearly supersede the original Pauli principle, which in this setting reads $\lambda_1 = 1$. This example revealed a dramatic effect of the skew symmetry condition on structure of the density matrix and provoked the authors’ emotional comment

“…We have no apology for consideration of such a special case. The general $N$-representability problem is so difficult and yet so fundamental for many branches of science that each concrete result is useful in shedding light on the nature of general solution.”

Shortly afterward Peltzer and Brandstatter [10] published a false solution, claiming that two-electrons, two-holes, and the Borland–Dennis system $\Lambda^3 \mathcal{H}_0$ are exceptional, and in all other cases the Pauli constraint $\lambda_1 \leq 1$ is the only one. After that the problem has stalled for more than three decades."1

Now, with a complete solution at hand, it may be appropriate to return back to physics and look for possible manifestations of the extended Pauli constraints.

Let me first give a sample of results for a three-electron system $\Lambda^3 \mathcal{H}_r$ of even or infinite rank $r$:

$$\lambda_{k+1} + \lambda_{r-k} \leq 1, \quad 0 \leq k < r;$$

(4)

$$\lambda_2 + \lambda_3 + \lambda_4 + \lambda_5 \leq 2, \quad \lambda_1 + \lambda_3 + \lambda_4 + \lambda_6 \leq 2;$$

(5)

$$\lambda_1 + \lambda_2 + \lambda_5 + \lambda_6 \leq 2, \quad \lambda_1 + \lambda_2 + \lambda_4 + \lambda_7 \leq 2;$$

(6)

1 Mostly because of lack a proper theoretical insight, that emerged much latter [11, 12, 13], and inconclusive results of numerical studies.
The inequalities (4) improve the original Pauli condition \( \lambda \leq 1 \). Due to normalization \( \text{Tr} \rho = 3 \) they turn into Borland–Dennis equations (3) for \( r = 6 \). The quadruple of inequalities (5) provides a full set of constraints for \( r \leq 7 \). A proper infinite extension of the last inequality in the quadruple is given by (6) where the differences between successive indices are natural numbers 1, 2, 3, 4, \ldots. Similar extensions for the other three constraints can be obtained by adding to them a tail of the series (6) starting with the term \( \lambda_{11} \).

A complete set of constraints heavily depends on the rank \( r \) and the number of particles. Currently they are known for all systems of rank \( \leq 10 \). To give an idea of complexity of the problem note that for systems \( \wedge^3 \mathcal{H}_{10} \), \( \wedge^4 \mathcal{H}_{10} \), \( \wedge^5 \mathcal{H}_{10} \) the constraints amount to 93, 125, 161 independent inequalities respectively.

**Pinned state effect.** Recall, that the Pauli principle is a purely kinematic constraint on available states of a multi-electron system. Not even a minuscule violation has been detected so far, in spite of numerous and increasingly sophisticated attempts [14]. Therefore whenever a dynamical trend is in conflict with Pauli constraints, the latter would prevail and the system eventually will be trapped in the boundary of the manifold of allowed states. This can manifest itself in degeneration some of the extended Pauli inequalities into equations. In this case the system and its state vector will be called pinned to the degenerate Pauli inequalities. Since a pinned system is primary driven by Pauli kinematics, rather than by Hamiltonian dynamics, it should be robust and remain pinned under a reasonably small variation of the Hamiltonian. This stability gives us a chance to detect pinned states and in a sense makes them real. A pinned system is essentially a new physical entity with its own dynamics and kinematics.

The concept can be illustrated by a string pendulum. For a small initial horizontal impulse at the lowest point its mass is confined to a circle. However, if the energy is big enough to raise the mass above the suspension point but is not sufficient to neutralize gravitation at the apex, then at some moment the string constraint becomes irrelevant and the mass switches into a free trajectory.

As a more relevant example, consider the first excited state of beryllium atom of spin \( S = 1 \) and \( S_z = 1 \). Here are its natural occupation numbers calculated from 10 spin-orbitals in the lowest three shells 1s, 2s, 2p [13].

\[
\begin{align*}
1.000000 & , 0.999995 & , 0.999287 & , 0.999284 & , 0.999711.
0.000007 & , 0.000009 & , 0.000007 & , 0.000000 & , 0.000000.
\end{align*}
\]  

(7)

Observe that the first orbital is completely filled and the last two are empty, i.e. the state is pinned to the initial Pauli constraints \( 0 \leq \lambda \leq 1 \). This kind of degeneration is very common. In its ultimate form it has been elevated to the *Aufbau* principle and incorporated into Hund’s rules.

The completely filled and empty orbitals are inactive, and therefore we effectively deal with a reduced system \( \wedge^3 \mathcal{H}_r \), in which all orbitals are partially filled. The extended Pauli constraints for this system amount to the quadruple of inequalities (5). Note that the exclusion principle itself \( \lambda_1 \leq 1 \) doesn’t enter into the list explicitly, but can be derived by taking sum of the second and third inequalities that gives \( \lambda_1 + \lambda_6 - \lambda_7 \leq 1 \). One can infer from this that the Pauli degeneration \( \lambda_1 = 1 \) for a system of this format would pin it to the last three constraints (6), that still fall short of \( \lambda_1 = 1 \). Actual calculation for beryllium data (7) shows that one of these three inequalities turns into exact equation

\[
\lambda_1 + \lambda_2 + \lambda_4 + \lambda_7 = 2,
\]  

and the other two are exact within a rounding error.

This equality stretches the Pauli principle to its limit, and therefore restricts the system’s kinematics. Recasting it into the form

\[
(a_1^\dagger a_1 + a_2^\dagger a_2 + a_4^\dagger a_4 + a_6^\dagger a_6) \Psi = 2 \Psi
\]  

(9)

we get a selection rule for Slater determinants \( |i, j, k = \psi_i \wedge \psi_j \wedge \psi_k | \) that enter into the decomposition \( \Psi = \sum \lambda_{ijk} |i, j, k \rangle \). Such a determinant should include two natural orbitals from the set \{1, 2, 4, 7\}, and one from its complement \{3, 5, 6\}. As a result the pinned system splits into two components \( \wedge^3 \mathcal{H}_4 \otimes \mathcal{H}_3 \), spanned by the above quadruple and triplet, and containing respectively two and one electron. The components can be readily identified with two spin-up electrons, and one spin-down.

The selection rules coming from the other two pinned inequalities bound the decomposition to four Slater determinants

\[
\Psi = \alpha |1, 2, 3 \rangle + \beta |1, 4, 5 \rangle + \gamma |1, 6, 7 \rangle + \delta |2, 4, 6 \rangle
\]  

(10)

with the amplitudes, up to phase factors, set by equations

\[
|\alpha|^2 = \lambda_3, \quad |\beta|^2 = \lambda_5, \quad |\gamma|^2 = \lambda_7, \quad |\delta|^2 = \lambda_6.
\]

This gives us an insight into structure of the pinned beryllium state whose form (10) should be stable under a perturbation. It corresponds to the type VII in Schouten classification of 3-vectors \( \Psi \in \wedge^3 \mathcal{H}_r \).

A similar consideration can be applied to the Borland-Dennis system \( \wedge^3 \mathcal{H}_6 \) in which every state is pinned by two equations (3). They reduce its internal kinematics to that of three qubits \( \mathcal{H}_2 \otimes \mathcal{H}_2 \otimes \mathcal{H}_2 \), each spanned by a couple of symmetric orbitals \( \psi_i, \psi_j, i + j = 7 \). In this interpretation the respective pairs of occupation numbers \( \lambda_5, \lambda_7 \) become spectra of three reduced states of \( \Psi \in \mathcal{H}_2 \otimes \mathcal{H}_2 \otimes \mathcal{H}_2 \), and the inequality (5) turns into Higuchi-Sudbery-Szulc compatibility condition [17].

**Spin-orbit interaction versus Pauli constraints.** In the above setting we were unable to address specific spin effects buried in join spin-orbital space \( \mathcal{H}_r = \mathcal{H}_s \otimes \mathcal{H}_s \).
Actually the orbital $\mathcal{H}_\ell$ and spin $\mathcal{H}_s$ degrees of freedom play very different rôle. The former, via Coulomb interaction, are primary responsible for dynamics, whereas the latter, disregarding a small relativistic correction, are purely kinematic. In this approximation the total spin is a good quantum number, that single out a specific component in Weyl’s decomposition
\begin{equation}
\wedge^N (\mathcal{H}_\ell \otimes \mathcal{H}_s) = \sum_{|\nu|=N} \mathcal{H}_\ell^\nu \otimes \mathcal{H}_s^\nu. \tag{11}
\end{equation}

Here $\mathcal{H}_\ell^\nu$ is an irreducible representation of the orbital group SU($\mathcal{H}_\ell$) defined by Young diagram $\nu$ and $\mathcal{H}_s^\nu$ is the representation of spin group SU($\mathcal{H}_s$) with transpose Young diagram $\nu^t$. The electron spin group is SU(2) and in this case $\nu$ is a two-column Young diagram. For example, in the ground closed-shell state of beryllium atom $\nu = \begin{pmatrix} 1 & 1 \end{pmatrix}$, while for the excited state of spin one $\nu = \begin{pmatrix} 1 & 1 \end{pmatrix}^t$. In general the total spin $S$ is equal to half-difference of lengths the two columns of $\nu$.

For spin resolved state $\Psi \in \mathcal{H}_\ell^\nu \otimes \mathcal{H}_s^\nu$ the Pauli constraints amount to inequalities between orbital $\lambda_i$ and spin $\mu_j$ natural occupation numbers normalized to traces $N$ and $I$ respectively [4]. As a toy example consider three electrons in $d$-shell (dim $\mathcal{H}_\ell = 5$) in low spin configuration $\nu = \begin{pmatrix} 1 & 1 \end{pmatrix}$ where the constraints are as follows [4, 6, 7]
\[
\begin{align*}
\lambda_1 + \frac{1}{2}(\lambda_4 + \lambda_5) &\leq 2, \\
\mu_1 &\leq 2(\lambda_1 - \lambda_2), \\
\mu_2 &\leq 2(\lambda_1 - \lambda_3), \\
\mu_3 &\geq 4\lambda_1 - 2\lambda_2 + 2\lambda_4 - 7.
\end{align*}
\]

Here $\mu = \mu_1 - \mu_2$ is spin magnetic moment in Bohr magnets, $\mu_B$ and I set $g = 2$ for the electron gyromagnetic factor.

The first inequality in the list improves the Pauli condition $\lambda_1 \leq 2$ for the number of electrons in an orbital.

The second line provides a kinematic upper bound on the spin magnetic moment. This contrasts sharply with prevailing opinion that the reduction of magnetic moment is a dynamical effect caused by spin-orbit coupling.\footnote{See for example [13, p.98]: “If spin-orbit interaction is zero free spin magnetism is realized. This is meant by saying that the orbital moment is quenched.”}

One has to be careful with the lower bound for $\mu = \mu_1 - \mu_2$ given in the last line. Recall, that $\mu_1, \mu_2$ are probabilities to find the system in spin-up and spin-down states with respect to some natural direction determined by leading eigenvector of the spin density matrix. It may not coincide with the direction of magnetic field $H$ used for measurement of the moment. However, for negligible spin-orbit coupling the natural direction is free to orient itself along the field to produce the maximal moment $\mu = \mu_1 - \mu_2$. Otherwise the coupling might reduce this ideal value to the level that breaks the Pauli constraint. This would be a signature of an appreciable spin-orbit interaction.

This example provides a key to an old puzzle about reduction of magnetic moment of a transition metal atom in a crystal, relative to its value in free space. I will focus below on body-centered cubic form of iron ($\alpha$-Fe), stable at normal condition, using a recent high precision $\gamma$-ray diffraction study by Jauch and Reehuis [19].

The study support an earlier finding [20], based on measurement of a Mössbauer shift, that the electron configuration of 3$d$-shell in iron crystal is $d^7$ rather than $d^6$ as for free atom. Such a modification of metallic 3$d$-shell is pretty common, albeit not universal. It reduces the maximal spin magnetic moment per atom from 4$\mu_B$ to 3$\mu_B$, while the experimental saturation moment is 2.22(1)$\mu_B$.

Recall, that in a crystal field of cubic symmetry the orbital moment is quenched and $d$-shell splits into two irreducible components of dimension 3 and 2 called $t_2g$ and $e_g$ subshells. The orbital density matrix retains the crystal symmetry, and therefore reduces to scalars $n_t$ and $n_e$ on the above subshells. As a result the orbital occupation numbers $\lambda = (n_t, n_t, n_t, n_e, n_e)$, $3n_t + 2n_e = 7$ depend only on one parameter $n_t$, where I expect $n_t \geq n_e$.

The Pauli constraints on spin magnetic moment $\mu$ versus the orbital occupation number $n_t$ for high spin $d^7$ configuration are shown in Fig.1. The plot also includes the experimental data for iron $\mu = 2.22, n_t = 1.458(7)$. The latter value is deduced from the relative number of $d$-electrons 62.5(3)% in $t_2g$ subshell [10].

The data suggest that the observed magnetic moment is the maximal one kinematically allowed by the electron density, i.e. the iron $d$-shell is pinned to the boundary segment $[A, B]$ given by equation $\mu = 7n_t - 8$. Let me stress again that the constraint on spin magnetic moment $\mu \leq 7n_t - 8$ comes from the kinematics of $d$-shell and has nothing to do with spin-orbit coupling. One can interpret it as an ultimate result of a multi-electron “exchange interaction”, though the term suggests a dynamical origin of the effect, while in fact it is purely kinematic.

The constraints shown in Fig.1 are actually derived from a system of 55 inequalities between orbital $\lambda_i$ and spin $\mu_j$ natural occupation numbers. The pentagon $ABCDE$ is a projection of a multidimensional polytope that includes all spin occupation numbers $\mu_i$, rather than just the total magnetic moment $\mu = 3\mu_1 + \mu_2 - \mu_3 - 3\mu_4$. It turns out, however, that the boundary segment $[A, B]$ has unique pull back $[\tilde{A}, \tilde{B}]$ in the bigger polytope
\[
\tilde{A} = \begin{pmatrix} 7 & 7 & 7 & 7 & 7 \end{pmatrix} \begin{pmatrix} 3 & 1 & 1 & 0 \end{pmatrix}, \quad \tilde{B} = \begin{pmatrix} 3 & 3 & 3 & 5 & 5 \end{pmatrix} \begin{pmatrix} 3 & 1 & 0 \end{pmatrix}
\]
where the first 5 components represent the orbital occupation numbers and the rest are spin ones. This allows to recover spin occupation numbers $\mu_i$ of iron $d$-shell
\[
\begin{pmatrix} 0.69, \ 0.23, \ 0.08, \ 0 \end{pmatrix}.
\]
The small probability 0.08 to have negative magnetic moment \(-1 \mu_B\) can be seen in a spin density plot \([22, p.170]\) built from polarized neutron scattering data. I wonder if the data contain enough information to recover the spin occupation numbers and verify the values \([12]\).

**Magnetovolume effect.** Pressure is an effective tool to change electronic structure, though apparently it remains detached from spin. This makes the observed reduction of magnetic moment under pressure a mystery, known as magnetovolume effect \([21]\). I use it below to test robustness of pinned iron states.

For \(\alpha\)-iron the magnetic moment is governed by the pinning equation \(\mu = 7n_t - 8\), at least when the pressure is not too high. If at some point the constraint would cease to exists, then the frozen degrees of freedom will be released and change the dynamics of the system. No such change is observed until a transition from bcc to hcp crystal structure has started. The magnetic moment at this point is about 1.9 \(\mu_B\) \([21]\) and the electron density should be close to spherical one \(n_e \approx n_{\alpha} \approx 1.4\) to accommodate the two incompatible symmetries. The transition actually passes through a phase coexistence interval. A linear extrapolation to the point where bcc phase vanishes gives the magnetic moment about 1.8 \(\mu_B\). This is consistent with the evolution along the pinning edge \([B, A]\).

The effect is more tricky in a face-centered cubic form of iron stable at high temperature or low density. It has two competing spin states, first conjectured by Weiss \([23]\). The one with high moment \(\mu \approx 2.5 \mu_B\) at some critical pressure collapses into a low spin one \(\mu \approx 1 \mu_B\).

Recall that 2.5 \(\mu_B\) is the maximal magnetic moment kinematically allowed for cubic iron, provided \(n_t \geq n_{\alpha}\). Assuming the latter condition we infer that the high spin state should be pinned to the point \(B\) and remains trapped at this point until one of the two pinning equations \(\mu = 7n_t - 8\) or \(\mu = 16 - 9n_t\) is released. As the above scenario suggests, at some critical pressure the first constraint is eventually freed and the state evolves along the segment \([B, C]\) into the low spin state \(C\), where it will be stabilized until the second pinning constraint \(\mu = 16 - 9n_t\) is relaxed. Then it slides along the path \([C, D]\) into a non-magnetic phase. This picture qualitatively fits the calculated \([24]\) and the observed \([25]\) evolutions and gives a hint about possible origin of the two spin states.

May be I have to conclude with a disclaimer that this letter is not about iron magnetism, used here as a testing ground for new concepts and methods originated from a recent advance in understanding of quantum kinematic constraints. Until now the kinematic effects were largely neglected or treated as dynamical ones. The confusion was clearly recognized by chemists \([20]\), and the above examples may support their objection. In the end, the role of Hamiltonian in some cases may reduce to pinning a state to a certain kinematic constraints which qualita-

![FIG. 1: Pauli constraints on spin magnetic moment (\(\mu_B\)) for 7 electrons in d-shell in cubic crystal field versus the occupation number \(n_t\) of a \(t_{2g}\) orbital. All points within the pentagon \(ABCDE\) are admissible. A black dot represents experimental data for iron.](image-url)
...then I offer no apologies as their kind of meat is unfortunately the chemists’ poison.” P. A. Cox, *Transition metal oxides*, Oxford Univ. Press, Oxford 1995, p. iv.