The Klyachko conditions from the chemical viewpoint

Carlos L. Benavides-Riveros

Nice, 8th November 2013

[joint work with J. M. Gracia-Bondía (Zaragoza) and M. Springborg (Saarbrücken)]
Pauli principle

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\psi_n \in \wedge^n \mathcal{H} \subset \mathcal{H} \otimes^n,
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where \( \mathcal{H} \) is the space of one electron.

- **Coleman (1963):** The set of admissible one-body RDM is given by:

\[ \rho_1 \geq 0, \quad \text{Tr} \rho_1 = n, \]

and the eigenvalues of \( \rho_1 \) (natural occupation numbers) obey \( 0 \leq \lambda_i \leq 1 \).

For a pure state \( [\rho_1]^i_k = \langle \Psi | a_i^\dagger a_k | \Psi \rangle \).
Additional constraints: Borland and Dennis (1972)

It has long been suspected that there are constraints **NOT** implied by the original Pauli principle on the spectrum of the one-body reduced density matrix \(\{\lambda_1, \lambda_2, \ldots\}\).

The system \(\wedge^3\mathcal{H}_6\) of three electrons and a six-dimensional one-particle Hilbert space exhibits the constraints

\[
\lambda_1 + \lambda_6 = \lambda_2 + \lambda_5 = \lambda_3 + \lambda_4 = 1, \quad \text{and} \\
d^6 := 2 - (\lambda_1 + \lambda_2 + \lambda_4) \geq 0 \quad \rightarrow \quad \lambda_1 + \lambda_2 \leq 1 + \lambda_3:
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Klyachko restrictions (2006)

Klyachko showed an algorithm to compute all such Pauli-like inequalities. For the general situation \( \wedge^n \mathcal{H}_m \), there is a finite set of generalized Pauli constraints:

\[
d^m_k = \kappa_0 + \kappa_1 \lambda_1 + \cdots + \kappa_n \lambda_n \geq 0, \quad \text{with} \quad \kappa_i \in \mathbb{Z}.
\]

For example, for \( \wedge^3 \mathcal{H}_7 \), there are four linear inequalities:

\[
\begin{align*}
d^7_1 &= 2 - (\lambda_1 + \lambda_2 + \lambda_4 + \lambda_7) \geq 0, \\
d^7_2 &= 2 - (\lambda_1 + \lambda_2 + \lambda_5 + \lambda_6) \geq 0, \\
d^7_3 &= 2 - (\lambda_2 + \lambda_3 + \lambda_4 + \lambda_5) \geq 0, \\
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Klyachko showed an algorithm to compute all such Pauli-like inequalities. For the general situation $\wedge^n\mathcal{H}_m$, there is a finite set of generalized Pauli constraints:

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For example, for $\wedge^3\mathcal{H}_7$, there are four linear inequalities:

$$d_1^7 = 2 - (\lambda_1 + \lambda_2 + \lambda_4 + \lambda_7) \geq 0, \quad d_2^7 = 2 - (\lambda_1 + \lambda_2 + \lambda_5 + \lambda_6) \geq 0,$$

$$d_3^7 = 2 - (\lambda_2 + \lambda_3 + \lambda_4 + \lambda_5) \geq 0, \quad d_4^7 = 2 - (\lambda_1 + \lambda_3 + \lambda_4 + \lambda_6) \geq 0.$$ 

The Klyachko restrictions are consistent, so lower rank ones can be derived from higher ones: putting $\lambda_7 = 0$ we obtain the former restrictions for $\wedge^3\mathcal{H}_6$. 

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The Klyachko conditions from the chemical viewpoint
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The tantalizing suggestion of the SCG paper is that the inequalities are *nearly saturated* in the ground state:

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When the inequalities are *completely saturated*

\[ d_k^m = \kappa_0 + \kappa_1 \lambda_1 + \cdots + \kappa_n \lambda_n = 0. \]

the number of Slater determinants needed for the description of a quantum mechanical system reduces significantly. This is the "pinning" phenomenon.
Pinning hopes: an example

For (say) a restricted spin configuration $\wedge^3 \mathcal{H}_6$ gives rise to:
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- **20** = $\binom{6}{3}$ Slater determinants in total.
- **9** of them are **eigenfunctions** of $S_z$, say ↓.
- **8** of them are moreover **eigenfunctions** of $S^2$ with $j = \frac{1}{2}$.

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Pinning hopes: another example

For $\gamma_2$ vs $\gamma_1$ with a restricted spin configuration here are in principle $(\begin{pmatrix} 7 \\ 3 \end{pmatrix}) = 35$ Slater determinants, of which 18 are spin-admissible.

The **pinned** system can be factorized

$$\gamma_2 \rightarrow H_3 \otimes \gamma_1 H_4,$$

not surprising since we are dealing with two electrons with spin $\downarrow$ (say) and one with spin $\uparrow$.

Assuming that $d_2^7 = 0$ then, the wave function can be reduced to 9 Slater determinants $[ijk]$, and if $d_3^7 = 0$, then to only 4:

$$\psi_{(3,7)} = a[123] + b[145] + c[267] + d[457].$$

With only double or triple excitations of the state [123]!
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\hat{H} = \sum_{i=1}^{3} \left( \frac{p_i^2}{2} + \frac{k}{2} x_i^2 \right) + \frac{D}{2} \sum_{i<j}^{3} (x_i - x_j)^2, \quad \psi_3 \in \wedge^3 (L^2(\mathbb{R})).
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Schilling, Gross, Christandl, PRL 110, 040404 (2013)
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The notion of quasipinning

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Parametrizing the coupling

$$\delta := \frac{3}{4} \frac{D}{k},$$

the spectrum is

$$1 - \lambda_1 = \frac{40}{729} \delta^6 - \frac{1390}{59049} \delta^8 + O(\delta^{10}),$$
$$1 - \lambda_2 = \frac{2}{9} \delta^4 - \frac{232}{729} \delta^6 + \frac{3926}{10935} \delta^8 + O(\delta^{10}),$$
$$1 - \lambda_3 = \frac{2}{9} \delta^4 - \frac{64}{243} \delta^6 + \frac{81902}{295245} \delta^8 + O(\delta^{10}),$$
$$\lambda_4 = \frac{2}{9} \delta^4 - \frac{64}{243} \delta^6 + \frac{73802}{295245} \delta^8 + O(\delta^{10}),$$
The notion of quasipinning

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$$0 \leq d^6 := 2 - (\lambda_1 + \lambda_2 + \lambda_4) = O(\delta^8) \quad \text{quasipinned!}$$
By the way...

If a quantum-mechanical system is quasipinned, what is the loss of information when projecting the total wave function onto the subspace of pinned states?
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Let $\psi_3 \in \wedge^3 \mathcal{H}_6$ and $P_6$ be the projection operator onto the pinned subspace $d^6 = 0$. Then, there are the following upper and lower bounds:

$$1 - \frac{1 + 2\xi}{1 - 4\xi} \cdot d^6 \leq \|P_6 \psi_3\|^2 \leq 1 - \frac{1}{2} d^6,$$

with $\xi := 3 - \lambda_1 - \lambda_2 - \lambda_3 < \frac{1}{4}$.

Schilling, Gross, Christandl, PRL 110, 040404 (2013)

Let $\psi_3 \in \wedge^3 \mathcal{H}_7$ and $P_7$ be the projection operator onto the pinned subspace $d^7_2 = 0$. Then, there are the following upper and lower bounds

$$1 - \frac{1 + 9\xi}{1 - 11\xi} \cdot d^7_2 \leq \|P_7 \psi_3\|^2 \leq 1 - \frac{1}{2} d^7_2,$$

with $\xi := 3 - \lambda_1 - \lambda_2 - \lambda_3 < \frac{1}{11}$.

CLBR, Gracia-Bondía, Springborg, PRA 88, 022508 (2013)

This is very small!
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For the helium-like functions, let us use the orthonormal basis in the classic by Shull and Löwdin:

\[
\delta_n(\alpha, r) := D_n \sqrt{\frac{\alpha^3}{\pi}} L_{n-1}^\zeta (2\alpha r) e^{-\alpha r}; \quad n = 1, 2, \ldots
\]

where \(D_n\) is a normalization constant, \(L_n^\zeta\) are the associated Laguerre polynomials and \(\langle \delta_m | \delta_n \rangle = \delta_n^m\). For the hydrogen-like we choose:

\[
\phi(\gamma, r) = \frac{1}{4} \sqrt{\frac{\gamma^5}{6\pi}} r e^{-\gamma r/2}.
\]

Shull, Löwdin, JChP 30, 617 (1959)
Lithium isoelectronic series: rank six

The lithium exact energy is $-7.478$ au. The H–F energy is $-7.432$ au; the variational energy of $[\delta_1 \downarrow \delta_1 \uparrow \phi \uparrow]$ is $-7.417$ au.

We consider two different approaches for obtaining six-rank approximations for lithium-like ions:
The occupation numbers of these systems are the following:

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For the constraints within our calculation $6^b$, we find

$$0 \leq d^{6^b} = \lambda_5 + \lambda_6 - \lambda_4 = 2.146 \times 10^{-5} \quad \text{and} \quad \frac{d^{6^b}}{\lambda_6} \approx 0.97$$

For the restricted spin orbital case $6^a$ one finds $d^{6^a} = 0$. 

*Pinning!!*
Lithium isoelectronic series: rank six, continued

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\textit{Pinning!!}

Nothing qualitatively changes for $\text{Be}^+, \text{B}^{++}, \text{C}^{+++} \ldots$
Lithium isoelectronic series: rank seven and eight

For the rank seven the Klyachko constraints read

\[ 0 \leq d_1^7 = 2 - (\lambda_1 + \lambda_2 + \lambda_4 + \lambda_7) = 0, \]
\[ 0 \leq d_2^7 = 2 - (\lambda_1 + \lambda_2 + \lambda_5 + \lambda_6) = 1.304 \times 10^{-5}, \]
\[ 0 \leq d_3^7 = 2 - (\lambda_2 + \lambda_3 + \lambda_4 + \lambda_5) = 7.741 \times 10^{-5}, \]
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TWO scales of quasipinning.
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**TWO scales** of quasipinning.

For \( ^3\mathcal{H}_8 \), there are 31 inequalities. Some of them are given by:

\[ 0 \leq d_i^8 = d_i^7 \quad i = 1, \ldots, 4 \]
\[ 0 \leq d_5^8 = 1 - (\lambda_1 + \lambda_2 - \lambda_3) \]
\[ 0 \leq d_6^8 = 1 - (\lambda_2 + \lambda_5 - \lambda_7) \]
\[ 0 \leq d_7^8 = 1 - (\lambda_1 + \lambda_6 - \lambda_7) \]
\[ 0 \leq d_8^8 = 1 - (\lambda_2 + \lambda_4 - \lambda_6) \]
\[ 0 \leq d_9^8 = 1 - (\lambda_1 + \lambda_4 - \lambda_5) \quad \text{and so on...} \]
The saturation of the polytope for the case of $\wedge^3 \mathcal{H}_8$ is given by:

THREE scales!
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THREE scales! In fact, four?
We have next studied the three-electron molecule $\text{He}_2^+$

Consider the **bonding** and **anti-bonding** wave functions:

$$\phi_g^s(r) = \frac{\phi^s_A(r) + \phi^s_B(r)}{\sqrt{2 + 2S}}$$

and

$$\phi_u^s(r) = \frac{\phi^s_A(r) - \phi^s_B(r)}{\sqrt{2 - 2S}}$$
where \( S = \langle \phi^s_A | \phi^s_B \rangle \), and the standard STO-3G basis set is given by the expression:

\[
\phi^s_X(r) = \sum_{i=1}^{3} c_i G^s_X(r, \alpha_i)
\]

with \( G^s_X(r, \alpha) = \alpha^{3/4} \pi^{-3/4} e^{-\frac{1}{2} \alpha |r-R_X|^2} \).

In this case, using the configuration

\[
[\phi^s_g \uparrow, \phi^s_g \downarrow, \phi^s_u \uparrow], \quad |R_A - R_B| = 2.06 \text{ a.u.}
\]

with the Slater orbital exponent \( \zeta \) equal to 1.833, we obtain for the ground state energy: \(-4.8459\) a.u. (pretty good).
Molecules III

Let us add two more spatial orbitals

\[
\chi_s^g(r) = \frac{\chi_s^A(r) + \chi_s^B(r)}{\sqrt{2 + 2S'}}; \\
\chi_s^u(r) = \frac{\chi_s^A(r) - \chi_s^A(r)}{\sqrt{2 - 2S'}}.
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Here

\[
\chi_X^s(r) = \sum_{i=1}^{3} c_i G_X^s(r, \beta_i).
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The occupation numbers of $\text{He}_2^+$ are the following:

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<td>0.001</td>
</tr>
</tbody>
</table>

For the constraints within our calculation $6^b$, we find

$$0 \leq d^{6^b} = \lambda_5 + \lambda_6 - \lambda_4 = 9.8 \times 10^{-8} \quad \text{and} \quad \frac{d^{6^b}}{\lambda_6} \approx 0.99$$

For the restricted determinant case $6^a$ one has $d^{6^a} = 0$ in this molecule example.

*Again, pinning*
Remarks on the coupled-cluster approximation

Size-consistency: the energy of system composed of a finite number of non-interacting subsystems must be equal to the energies of such subsystems calculated separately:

\[ E(AB) = E(A) + E(B). \]

Size-extensivity: the energy of a non-interacting system must scale correctly with the size of the system:

\[ E(nA) = nE(A). \]

The configuration interaction (CI) wave function

\[ |\psi_{CI}\rangle = \left( 1 + \sum_{r,\mu} c_{\mu r} a_{r}^\dagger a_{\mu} + \sum_{r<s,\mu<v} c_{\mu r,\nu s} a_{r}^\dagger a_{s}^\dagger a_{\mu} a_{\nu} + \cdots \right) |\psi_0\rangle \]

is exact in the full CI limit, but lacks size-extensivity with any truncation of the configuration space.
Remarks on the coupled-cluster approximation

The basic idea in coupled cluster theory with double excitations (CCD) consists in considering the ansatz

$$|\psi_{\text{CCD}}\rangle = e^{\hat{T}_2} |\psi_0\rangle,$$

where

$$\hat{T}_2 = \sum_{r<s, \mu<\nu} c_{\mu\nu} a_r^+ a_s^+ a_{\mu} a_{\nu},$$

is the operator for double excitations.
Remarks on the coupled-cluster approximation

The natural occupation numbers of the double excited wave function in $\wedge^3 \mathcal{H}_7$

$$\psi_{\text{CCD}} = a[123] + b[245] + c[267] + d[367]$$

$$+ e([246] - [146]) + f([347] - [356]) + g([146] - [247])$$

with $\hat{S}_z \psi_{\text{CCD}} = -\frac{1}{2} \psi_{\text{CCD}}$ and $\hat{S}^2 \psi_{\text{CCD}} = \frac{3}{4} \psi_{\text{CCD}}$

satisfy the relations

$$d_1^7 = 2 - \lambda_1 - \lambda_2 - \lambda_4 - \lambda_7 = 0 \quad \text{and}$$

$$d_2^7 = 2 - \lambda_1 - \lambda_2 - \lambda_5 - \lambda_7 = 2|e|^2.$$ 

When $e = 0$, the system is pinned.
Remarks on the coupled-cluster approximation

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When $e = 0$, the system is pinned.

Our conjecture is that pinned wave functions belongs to the set of double excited wave functions.
Remarks on the coupled-cluster approximation

“A pinned system is essentially a new physical entity with its own dynamics and kinematics“.


- **Single** excitations do not mix *directly* with the HF ground state: $\langle S|H|\psi_0 \rangle = 0$.
- They can be expected to have a very small effect on the ground state energy.
- **Double** excitations mix *directly* with the HF ground state.
- It is to be expected that they play an important role in determining the correlation energy.
In general the nonrelativistic QM of an electronic system is driven by the Hamiltonian

\[ H = T + V_{\text{ext}} + V_{\text{ee}} = \sum_{i=1}^{n} \frac{1}{2} \Delta \vec{q}_i + \sum_{i=1}^{n} V(\vec{q}) + \sum_{i<j}^{n} \frac{1}{|\vec{q}_i - \vec{q}_j|}. \]

Pure states \( \gamma_n := |\psi \rangle \langle \psi| \) have skewsymmetric \( \psi(x_1, \ldots, x_n) \), with \( x_i = (\vec{q}_i, \varsigma_i) \), spatial and spin variables.

Integrating out \( x_3, \ldots, x_n \) gives the 2-body Reduced Density Matrix \( \gamma_2(x_1, x_2; x_1', x_2') \)

\[ \binom{n}{2} \int \gamma_n(x_1, x_2, x_3, \ldots, x_n; x_1', x_2', x_3, \ldots, x_n) \, dx_3 \ldots dx_n. \]

We have the general sum rule: \( \gamma_1 = \frac{2}{n-1} \int \gamma_2 \, dx_2. \)
We are interested in the ground state energy of the system. There is the helium-like energy functional:

\[ \mathcal{E}(\gamma_2) = \text{Tr} \left\{ \left[ -\frac{2}{N-1} \left( \frac{\Delta \vec{q}_1}{2} + \frac{Z}{|\vec{q}_1|} \right) + \left( \frac{1}{|\vec{q}_1 - \vec{q}_2|} \right) \right] \gamma_2 \right\}. \]

The ground-state energy minimizes \( \mathcal{E}(\gamma_2) \):

\[ E_{gs} = \min \{ \mathcal{E}(\gamma_2) \mid \gamma_2 \in B_n^2 \}. \]
We are interested in the ground state energy of the system. There is the helium-like energy functional:

$$\mathcal{E}(\gamma_2) = \text{Tr} \left\{ -\frac{2N}{2(N-1)} \left( \frac{\Delta \tilde{q}_1}{2} + \frac{Z}{|\tilde{q}_1|} \right) + \left( \frac{1}{|\tilde{q}_1 - \tilde{q}_2|} \right) \right\} \gamma_2. $$

The ground-state energy minimizes $\mathcal{E}(\gamma_2)$:

$$E_{gs} = \min \{ \mathcal{E}(\gamma_2) | \gamma_2 \in \mathcal{B}_n^2 \}. $$

Here,

$$\gamma_2 \in \mathcal{B}_n^2 \iff \exists \gamma_n \in \text{DM}_n : \gamma_2 = \binom{n}{2} \int \gamma_n \, dx_3 \ldots dx_n,$$

where $\text{DM}_n$ is the set of the $n$-particle density matrices. In general, the N-representability problem consists in finding necessary and sufficient conditions for the set of admissible $\gamma_2$, namely: $\mathcal{B}_n^2$. 

Something is already known

Consider a quantum system composed of $n$ fermions. A two-body RDM is a fermionic density matrix if it is

- Hermitian,
- normalized (fixed trace),
- antisymmetric under the exchange of particles, and
- positive semidefinite $\iff$ its eigenvalues are non-negative.

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In the coordinate-space representation

$$\gamma_2(x_1, x_2; x_1', x_2') = \sum_{ijkl} \Gamma_{kl}^{ij} f_i^*(x_1') f_j^*(x_2') f_k(x_1) f_l(x_2),$$

where

$$\Gamma_{kl}^{ij} = \langle \psi | a_i^+ a_j^+ a_l a_k | \psi \rangle.$$
Consider a quantum system composed of \( n \) fermions. A two-body RDM is a fermionic density matrix if it is

- Hermitian, \( \Gamma = \Gamma^* \)
- normalized (fixed trace), \( \sum_{ik} \Gamma^{ik}_{ik} = \binom{n}{2} \)
- antisymmetric \( \Gamma^{ij}_{kl} = -\Gamma^{ij}_{lk} = -\Gamma^{ji}_{kl} \)
- positive semidefinite \( \iff \) its eigenvalues are non-negative. \( \Gamma \geq 0 \)

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$$\Gamma \succeq 0 \quad G \succeq 0 \quad Q \succeq 0 \quad T_1 \succeq 0 \quad T_2 \succeq 0$$
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Garrod and Percus (1964): The $G$ and $Q$ conditions establish that the following two matrices

$$G^{ij}_{kl} = \langle \psi | a_i^\dagger a_j^\dagger a_k a_l | \psi \rangle \quad \text{and} \quad Q^{ij}_{kl} = \langle \psi | a_i a_j a_l^\dagger a_k^\dagger | \psi \rangle,$$

must be positive semidefinite if $\gamma_2$ is N-representable.
G, Q, T1 and T2 conditions

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**Erdhal (1978):** The other known N-representability conditions are the \( T_1 \) and \( T_2 \) conditions:

\[ T_{1lmn}^{ijk} := \langle \psi | a_i^\dagger a_j^\dagger a_k a_n a_m a_l + a_n a_m a_l a_i^\dagger a_j^\dagger a_k^\dagger | \psi \rangle \geq 0 \]

\[ T_{2lmn}^{ijk} = \langle \psi | a_i^\dagger a_j^\dagger a_k a_n a_m a_l + a_n^\dagger a_m a_l a_i^\dagger a_j^\dagger a_k | \psi \rangle \geq 0 \]
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Mazziotti (2012): A constructive solution of the N-representability problem based in a hierarchy of constraints. In addition to the above conditions there is a bigger set of conditions: \( \hat{T}_2, \tilde{T}_2, \ldots \)
G, Q, T1 and T2 conditions

If a matrix $O$ is positive semidefinite, its diagonal elements are non-negative.
G, Q, T1 and T2 conditions

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Then, in particular,

$$\Gamma_{ij} \geq 0, \quad G_{ij} \geq 0, \quad Q_{ij} \geq 0, \quad T_{1ijk} \geq 0, \quad T_{2ijk} \geq 0, \quad \tilde{T}_{2ijk} \geq 0, \quad \tilde{T}_{2ijk} \geq 0$$
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which implies, among other relations,

$$\lambda_i \geq \Gamma_{ij}$$

$$1 - \lambda_i - \lambda_j \geq -\Gamma_{ij}$$

$$1 - \lambda_i - \lambda_j - \lambda_k \geq -\Gamma_{ij} - \Gamma_{ik} - \Gamma_{jk}$$

$$\lambda_i + \Gamma_{jk} \geq \Gamma_{ij} + \Gamma_{ik}$$

In particular, $1 - \lambda_1 - \lambda_2 + \lambda_3 \geq \lambda_3 - \Gamma_{12} \geq 0$. 
"A pinned system is essentially a new physical entity with its own dynamics and kinematics".


For pinned states in $\wedge^3 \mathcal{H}_7$ such that: $1 - \lambda_1 - \lambda_2 + \lambda_3 = 0$ the spectra of the $T_1$ and $T_2$ matrices are trivial:

$$\text{Spec}(T_1) = \{1, 1, 0, 0, 0, 0, 0, 0\}$$

$$\text{Spec}(T_2) = \{1, 1, 1, 1, 1, 1, 0, 0, 0, \ldots\}$$

work in progress...
Summary

- We have checked Klyachko constraints in a simple atomic model.
- We have checked Klyachko constraints in a simple molecular model.
- We have examined the Klyachko relations in the light of CCD theory.
- An investigation is currently in progress aimed to establish the connections between Klyachko and Mazziotti paradigms.