UNIQUENESS OF NMR SPECTRAL ANALYSIS FOR A GENERAL SYSTEM OF NUCLEI WITH SPIN NUMBER 1/2

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An upper estimate is found for the smallest number of sets of assigned experimental frequencies (corresponding to different intensities of external magnetic field) necessary for a unique solution of the general spin (spin number 1/2) inverse secular problem. The proof of uniqueness can in principle be used as a direct method of calculation of NMR parameters.

The calculation of chemical shifts and spin-spin coupling constants (NMR parameters) for a general system of nuclei from assigned experimental frequencies leads, in general, to a system of nonlinear equations. The set of all solutions of this system corresponding to a set of resonance frequencies obtained by measurement at a single external magnetic field intensity contains generally several real, *i.e.* physically plausible solutions[1,2]. Hence follows the necessity in practical calculations to apply additional information (equations) enabling one to select from all real solutions the one that is physically correct. In our previous work[3,4], we considered as additional information sets of resonance frequencies obtained at other, generally different, intensities of external magnetic field, and for special cases of systems ABC and AA'BB' we proved that their measurement at two intensities is a sufficient condition for the uniqueness of the solved problem.

The present paper brings (except for certain "singular" cases discussed in a subsequent section) an explicit calculation of chemical shifts and spin-spin coupling constants for a general system of $n \geqq 4$ magnetically nonequivalent nuclei (spin number 1/2) from a set of assigned resonance frequencies obtained by measurement at $[\frac{1}{2}\binom{n}{2} - \frac{1}{2}] + 1$ different external magnetic field intensities.*

RESULTS

The computation of NMR parameters for the above-mentioned nuclear systems from sets of resonance frequencies corresponding to T values of external magnetic field intensities consists in solving the following system of algebraic equations[3]:

$$Tr\{(\mathbf{H}_l(k_t))^{\alpha_l}\} = \sum_{\beta_l=1}^{p} (E_{l,\beta_l}(k_t))^{\alpha_l} \qquad (1)$$

* The symbol $[x]$ is used to denote the largest integer smaller or equal to x.

($l = 0,1,\ldots,n$; $\alpha_l = 1,2,\ldots,\binom{n}{l}$, $p = \binom{n}{l}$, $t = 1,2,\ldots,T$), where $\boldsymbol{H}_l(k_t)$ denotes submatrices of matrix $\boldsymbol{H}$ of the spin Hamiltonian. Elements of the matrix $\boldsymbol{H}$ are, in the basis of spin product functions, given by[5,6]

$$\{\boldsymbol{H}_l(k_t)\}_{\mathbf{x},\mathbf{x}} = \tfrac{1}{2}k_t \sum_{p=1}^{n} \nu_p x_p + \tfrac{1}{4}\sum_{p=1}^{n-1} \sum_{q=p+1}^{n} J_{pq} x_p x_q \,, \tag{2}$$

$$\{\boldsymbol{H}_l(k_t)\}_{\mathbf{x},\mathbf{y}} = \begin{cases} \tfrac{1}{2} J_{pq} & \text{for } \mathbf{x} \text{ and } \mathbf{y} \text{ differing just in 2 coordinates,} \\ 0 & \text{in other cases.} \end{cases}$$

For the same l the row index $\mathbf{x}$ and, also independently the column index $\mathbf{y}$ are set equal in turn to all elements of $D_{n,l}$ which is the set of all n-dimensional vectors having l coordinates equal to $+1$ and $n - l$ coordinates equal to -1; $E_{l,\beta_l}(k_t)$ denotes energy levels defined uniquely by the corresponding experimental frequencies, obtained by measurement in external magnetic fields characterized[3] by the coefficients k_t.

In solving the given problem, the following principle is utilized: Equations corresponding only to submatrices $\boldsymbol{H}_0$, $\boldsymbol{H}_1$, $\boldsymbol{H}_2$, $\boldsymbol{H}_{n-2}$, $\boldsymbol{H}_{n-1}$ and $\boldsymbol{H}_n$ are selected from the system (*1*) and an integer T is determined for which this restricted system has already a unique solution (which is obviously also a solution of the original system). The NMR parameters are determined in two steps: first the chemical shifts ν_i are found (*cf.* theorem *1*) and then the coupling constants J_{ij} either with the aid of theorem *2* (for $n = 4$) or theorem *3* (for $n > 4$).

Theorem 1

Let $n \geqq 4$; let us consider real nonzero numbers $k_1, k_2, \ldots, k_T$, where $T = [n/2] + 1$, and numbers $E_{l,\beta_l}(k_t)$, where $\beta_l = 1,2,\ldots,\binom{n}{l}$; $l = 0,1,2,\ldots,n$. Let the following conditions be fulfilled: *a*) $k_r^2 \neq k_s^2$ ($r \neq s$), *b*) the system (*1*) has for k_t and $E_{l,\beta_l}(k_t)$ a solution (ν_j, J_{ij}). Then there exists (disregarding arbitrary permutations of indexes $1,2,\ldots,n$) a single n-tuple ($\nu_1,\nu_2,\ldots,\nu_n$) and numbers J_{ij} so that the solution is (ν_i, J_{ij}). (According to ref.[3], this theorem applies also to the case $n = 3$.)

Theorem 2

Let $n = 4$; let us consider nonzero numbers k_1, k_2 and k_3 (*i.e.* $T = 3$) and numbers $E_{l,\beta_l}(k_t)$, where $\beta_l = 1,2\ldots\binom{4}{l}$; $l = 0,1,\ldots 4$; $t = 1,2,3$, and let the following conditions be fulfilled: *a*) $k_r^2 \neq k_s^2$ ($r \neq s$), *b*) the system (*1*) for $n = 4$ has a solution ($\nu_1, \nu_2, \ldots, \nu_4, J_{12}, \ldots, J_{34}$) for which $\nu_r \neq \nu_s$. Then the system (*1*) has a single solution ($\nu_1, \ldots, \nu_4, J_{12}, \ldots, J_{34}$) (again disregarding arbitrary permutations of indexes $1-4$).

Theorem 3

Let $n > 4$ be an integer; let us consider nonzero numbers $k_1, \ldots, k_T$, where $T = [\frac{1}{2}\binom{n}{2} - \frac{1}{2}] + 1$, and numbers $E_{l,\beta_l}(k_t)$, where $\beta_l = 1,2, \ldots, \binom{n}{l}$; $l = 0,1, \ldots, n$; $t = 1,2, \ldots, T$; and let the following conditions apply: *a*) $k_r^2 \neq k_s^2$ $(r \neq s)$, *b*) the system (*1*) has a solution (v_i, J_{ij}) for which $v_i + v_j \neq v_{i'} + v_{j'}$ $((i, j) \neq (i', j')$, $1 \leqq i \leqq j \leqq n$, $1 \leqq i' \leqq j' \leqq n)$. Then the system (*1*) has a single solution (v_i, J_{ij}) (again disregarding permutations of indexes).

PROOFS

Proof of theorem 1: An algebraic equation of *n*-th degree is found the roots of which are $v_1, \ldots, v_n$. We define

$$\mathbf{G}_1(k_t) = \mathbf{H}_1(k_t) + (\tfrac{1}{2}k_t \sum_{j=1}^{n} v_j - \tfrac{1}{4} \sum_{1 \leqq i < j \leqq n} J_{ij})\, \mathbf{I}^{(n)}\,,$$

$$\mathbf{G}_{n-1}(k_t) = -\mathbf{H}_{n-1}(k_t) + (\tfrac{1}{2}k_t \sum_{j=1} v_j + \tfrac{1}{4} \sum_{1 \leqq i < j \leqq n} J_{ij})\, \mathbf{I}^{(n)}\,,$$

where $\mathbf{I}^{(n)}$ denotes an $n \times n$ unit matrix. The system (*1*) implies that the matrix $\mathbf{G}_1(k_t)$ has eigenvalues $F_{1,\beta_1}(k_t) = E_{1,\beta_1}(k_t) - E_{0,1}(k_t)$, $\beta_1 = 1,2, \ldots, n$, $t = 1,2, \ldots, [n/2] + 1$, and the matrix $\mathbf{G}_{n-1}(k_t)$ has eigenvalues $F_{n-1,\beta_{n-1}}(k_t) = - E_{n-1,\beta_{n-1}}(k_t) + E_n(k_t)$, $\beta_{n-1} = 1,2, \ldots, n$ and $t = 1,2, \ldots, [n/2] + 1$. From this we obtain the following system of equations:

$$Tr[(\mathbf{G}_l(k_t))^{\alpha_l}] = M_{l,\alpha_l}(k_t)\,, \tag{3}$$

where

$$M_{l,\alpha_l} = \sum_{\beta_l=1}^{n} (F_{l,\beta_l}(k_t))^{\alpha_l} \quad (l = 1, n - 1; \alpha_l = 1,2, \ldots, n).$$

The matrices $\mathbf{G}_1(k_t)$ and $\mathbf{G}_{n-1}(k_t)$ can be written uniquely in the form

$$\mathbf{G}_1(k_t) = k_t\mathbf{R} + \mathbf{S}\,, \quad \mathbf{G}_{n-1}(k_t) = k_t\mathbf{R} - \mathbf{S}\,, \tag{4}$$

where the matrices $\mathbf{R}$ and $\mathbf{S}$ do not depend on k_t. On introducing Eqs (*4*) into (*3*) we obtain the system of equations

$$\sum_{\sigma=0}^{\alpha_1} \binom{\alpha_1}{\sigma} k_t^{\alpha_1-\sigma}\, Tr(\mathbf{R}^{\alpha_1-\sigma}\mathbf{S}^{\sigma}) = M_{1,\alpha_1}(k_t)\,, \tag{5}$$

$$\sum_{\sigma=0}^{\alpha_n-1} \binom{\alpha_{n-1}}{\sigma} (-1)^{\sigma}\, k_t^{\alpha_{n-1}-\sigma}\, Tr\,(\mathbf{R}^{\alpha_{n-1}-\sigma}\mathbf{S}) = M_{n-1,\alpha_{n-1}}(k_t)\,. \tag{6}$$

Summing these equations for an equal index t and $\alpha_1 = \alpha_{n-1}$ one obtains

$$2 \sum_{\substack{\sigma=0 \\ \sigma \text{ even}}}^{\alpha} \binom{\alpha}{\sigma} k^{\alpha-\sigma} \, Tr\left(\mathbf{R}^{\alpha-\sigma}\mathbf{S}^{\sigma}\right) = M_{1,\alpha}\, k_t) + M_{n-1,\alpha}(k_t), \tag{7}$$

where $\alpha = 1,2, \ldots, n$ and $t = 1,2, \ldots, [n/2] + 1$. From the system (7) it follows that

$$Tr(\mathbf{R}^{\alpha}) = P_{\alpha} \tag{8}$$

for

$$P_{\alpha} = \tfrac{1}{2} \left| M_{1,\alpha}(k_t) + M_{n-1,\alpha}(k_t),\, k_t^{\alpha-2}, \ldots, k_t^{\alpha-2[\alpha/2]} \right| / \left| k_t^{\alpha}, k_t^{\alpha-2}, k_t^{\alpha-4}, \ldots, k_t^{\alpha-2[\alpha/2]} \right| ,$$

where the row index $t = 1,2, \ldots, [a/2] + 1$ and $\alpha = 1,2, \ldots, n$. From the assumption *a*) in theorem 1 it follows that the determinant in the denominator is nonzero. By calculating the matrix $\mathbf{R}$ we find easily that

$$Tr(\mathbf{R}^{\alpha}) = \sum_{j=1}^{n} v_j^{\alpha} . \tag{9}$$

On combining Eqs (8) and (9) we obtain a system of n equations for the chemical shifts $v_1, \ldots, v_n$. The theory of symmetrical polynomials[6] implies that this system has a single solution $(v_1, \ldots, v_n)$ disregarding permutations of indexes; v_j is taken to mean roots of the algebraic equation $v^n + C_1 v^{n-1} + C_2 v^{n-2} + \ldots + C_n = 0$, where $C_1 = - P_1$ and $C_{\gamma} = - (P_{\gamma} + C_1 P_{\gamma-1} + \ldots + C_{\gamma-1} P_1)/\gamma$, $\gamma = 2,3, \ldots, n$. The proof is accomplished.

Proof of theorem 2: Theorem *1* ensures that the system (*1*) for $n = 4$ is uniquely solvable with respect to the chemical shifts (v_1, v_2, v_3, v_4). If these are introduced into the system (*1*) one obtains for the coupling constants $J_{12}, J_{13}, \ldots, J_{34}$ a system of equations to which, as we shall show now, a unique solution exists. From Eqs (5) and (6) for $n = 4$ it follows after a simple rearrangement:

$$Tr(\mathbf{R}^{\sigma}\mathbf{S}) = T_{\sigma} , \quad \sigma = 0,1,2,3 , \tag{10}$$

where

$$T_0 = (M_{1,1}(k_1) - M_{3,1}(k_1))/2 , \quad T_1 = (M_{1,2}(k_1) - M_{3,2}(k_1))/4k_1 ,$$

$$T_2 = (M_{1,3}(k_1) - M_{3,3}(k_1) - M_{1,3}(k_2) + M_{3,3}(k_2))/6(k_1^2 - k_2^2) \quad \text{and}$$

$$T_3 = ((M_{1,4}(k_1) - M_{3,4}(k_1))\, k_2 - (M_{1,4}(k_2) - M_{3,4}(k_2))\, k_1)/8k_1k_2(k_1^2 - k_2^2) .$$

With regard to the form of the matrices **R** and **S** the system (*10*) can be rewritten in the form

$$\hat{J}_1 v_1^\sigma + \hat{J}_2 v_2^\sigma + \hat{J}_3 v_3^\sigma + \hat{J}_4 v_4^\sigma = -2T_\sigma, \quad \sigma = 0,1,2,3, \qquad (10a)$$

where

$$\hat{J}_r = \sum_{\rho=1}^{r-1} J_{\rho r} + \sum_{\rho=r+1}^{4} J_{r\rho} \quad r = 1,2,3,4. \qquad (11)$$

It follows from the system (*10a*) that $\hat{J}_1 = -2\Delta^{-1}|T_\alpha, v_2^\alpha, v_3^\alpha, v_4^\alpha|, \ldots, \hat{J}_4 = -2\Delta^{-1}|v_1^\alpha, v_2^\alpha, v_3^\alpha, T_\alpha|$ ($\alpha = 0,1,2,3$), where

$$\Delta = |v_\alpha^\beta|_{\alpha=1,2,3,4}^{\beta=0,1,2,3} = (v_1 - v_2)(v_1 - v_3)\ldots(v_3 - v_4) \neq 0.$$

Hence, Eq. (*11*) represents four independent equations for the coupling constants J_{ij}; other ones are obtained with the aid of submatrices $\mathbf{H}_2(k_t)$, which can be uniquely expressed as $\mathbf{H}_2(k_t) = k_t\mathbf{C} + \mathbf{D}$. The matrices **C** and **D** are independent of k_t and besides fulfil the following lemma (for proof see Appendix):

Lemma 1: Let r and s be nonnegative integers, r odd. Then $Tr(\mathbf{C}^r\mathbf{D}^s) = 0$.

Starting from the system (*1*) for $n = 4$, $l = 2$, $\alpha_l = 1,3,5$, we obtain with the use of lemma *1* the following system of equations:

$$Tr(\mathbf{D}) = W_0, \quad 3k_t^2\, Tr(\mathbf{C}^2\mathbf{D}) + Tr(\mathbf{D}^3) = Y(k_t)$$

$$5k_t^4\, Tr(\mathbf{C}^4\mathbf{D}) + 10k_t^2\, Tr(\mathbf{C}^2\mathbf{D}^3) + Tr(\mathbf{D}^5) = Z(k_t) \qquad (12)$$

where

$$W_0 = \sum_{j=1}^{6} E_{2,j}(k_1), \quad Y(k_t) = \sum_{j=1}^{6} (E_{2,j}(k_t))^3, \quad Z(k_t) = \sum_{j=1}^{6} (E_{2,j}(k_t))^5.$$

It follows from (*12*) that

$$Tr(\mathbf{C}^{2\varepsilon}\mathbf{D}) = W_\varepsilon, \quad \varepsilon = 0,1,2, \qquad (13)$$

where $W_1 = (Y(k_1) - Y(k_2))/3(k_1^2 - k_2^2)$ and $W_2 = (Z(k_1)(k_2^2 - k_3^2) + Z(k_2) \cdot (k_3^2 - k_1^2) + Z(k_3)(k_1^2 - k_2^2))/5(k_1^2 - k_2^2)(k_1^2 - k_3^2)(k_2^2 - k_3^2)$. Further we set

$$\mu_1 = (-v_1 - v_2 + v_3 + v_4)/2, \quad \mu_2 = (-v_1 + v_2 - v_3 + v_4)/2,$$

$$\mu_3 = (-v_1 + v_2 + v_3 - v_4)/2, \qquad (14)$$

$$\tilde{J}_1 = \tfrac{1}{4}(J_{12} - J_{13} - J_{14} - J_{23} - J_{24} + J_{34}),$$
$$\tilde{J}_2 = \tfrac{1}{4}(-J_{12} + J_{13} - J_{14} - J_{23} + J_{24} - J_{34}),$$
$$\tilde{J}_3 = \tfrac{1}{4}(-J_{12} - J_{13} + J_{14} + J_{23} - J_{24} - J_{34}). \qquad (15)$$

With regard to the form of matrices **C** and **D**, the system (*13*) can be rewritten in the form

$$\tilde{J}_1\mu_1^{2\varepsilon} + \tilde{J}_2\mu_2^{2\varepsilon} + \tilde{J}_3\mu_3^{2\varepsilon} = \tfrac{1}{2}W_\varepsilon \quad (\varepsilon = 0,1,2).$$

The determinant of this system, $D = (\mu_1^2 - \mu_2^2)(\mu_1^2 - \mu_3^2)(\mu_2^2 - \mu_3^2)$, is according to our assumption different from zero, hence $\tilde{J}_1 = (1/2D)|W_\alpha, \mu_2^\alpha, \mu_3^\alpha|$, $\tilde{J}_2 = (1/2D)|\mu_1^\alpha, W_\alpha, \mu_3^\alpha|$, and $\tilde{J}_3 = (1/2D)|\mu_1^\alpha, \mu_2^\alpha, W_\alpha|$ $(\alpha = 0,1,2)$. On combining Eqs (*11*) and (*15*) we obtain the following system of linear equations for the coupling constants J_{ij}:

$$\begin{array}{l}
J_{12} + J_{13} + J_{14} + 0 + 0 + 0 = \hat{J}_1 \\
J_{12} + 0 + 0 + J_{23} + J_{24} + 0 = \hat{J}_2 \\
0 + J_{13} + 0 + J_{23} + 0 + J_{34} = \hat{J}_3 \\
0 + 0 + J_{14} + 0 + J_{24} + J_{34} = \hat{J}_4 \\
J_{12} - J_{13} - J_{14} - J_{23} - J_{24} + J_{34} = 4\tilde{J}_1 \\
-J_{12} + J_{13} - J_{14} - J_{23} + J_{24} - J_{34} = 4\tilde{J}_2 \\
-J_{12} - J_{13} + J_{14} + J_{23} - J_{24} - J_{34} = 4\tilde{J}_3
\end{array}$$

whence it follows that $\hat{J}_1 + \hat{J}_2 + \hat{J}_3 + \hat{J}_4 = -8(\tilde{J}_1 + \tilde{J}_2 + \tilde{J}_3)$ and

$$J_{12} = \tfrac{1}{2}(\hat{J}_1 + \hat{J}_2) + \tilde{J}_1 - A, \quad J_{34} = -\tfrac{1}{2}(\hat{J}_1 + \hat{J}_2) + \tilde{J}_1 + 3A,$$
$$J_{13} = \tfrac{1}{2}(\hat{J}_1 + \hat{J}_3) + \tilde{J}_2 - A, \quad J_{24} = -\tfrac{1}{2}(\hat{J}_1 + \hat{J}_3) + \tilde{J}_2 + 3A,$$
$$J_{14} = \tfrac{1}{2}(\hat{J}_1 + \hat{J}_4) + \tilde{J}_3 - A, \quad J_{23} = -\tfrac{1}{2}(\hat{J}_1 + \hat{J}_4) + \tilde{J}_3 + 3A,$$

where $A = -(\tilde{J}_1 + \tilde{J}_2 + \tilde{J}_3)$. The proof of theorem *2* is accomplished.

Proof of theorem 3: For $n > 4$ we have $[\frac{1}{2}\binom{n}{2} - \frac{1}{2}] + 1 > [n/2] + 1$ so that the assumptions of theorem *3* involve those of theorem *1*. Hence, in the sense of theorem *1* a unique n-tuple of chemical shifts $(\nu_1, \nu_2, \ldots, \nu_n)$ exists (disregarding permutations of indexes) and so for a complete proof only the determination of the coupling constants J_{ij} is necessary. To this purpose we use the submatrices $\mathbf{H}_2(k_t)$ and $\mathbf{H}_{n-2}(k_t)$, which can be uniquely expressed as

$$\mathbf{H}_2(k_t) = -k_t\mathbf{U} + \mathbf{V}, \quad \mathbf{H}_{n-2}(k_t) = k_t\mathbf{U} + \mathbf{V}, \qquad (16), (17)$$

where the matrices $\mathbf{U}$ and $\mathbf{V}$ are independent of k_t. On introducing these equations into *(1)* we obtain for $l = 2$ and $n - 2$ the system

$$\sum_{\sigma=0}^{\alpha} \binom{\alpha}{\sigma} k_t^{\alpha-\sigma}(-1)^\sigma \, Tr(\mathbf{U}^{\alpha-\sigma}\mathbf{V}) = M_{2,\alpha}(k_t), \qquad (18)$$

$$\sum_{\sigma=0}^{\alpha} \binom{\alpha}{\sigma} k_t^{\alpha-\sigma} \, Tr(\mathbf{U}^{\alpha-\sigma}\mathbf{V}) = M_{n-2,\alpha}(k_t), \qquad (19)$$

where $\alpha = 1,2, \ldots, \binom{n}{2}$, and with $p = \binom{n}{2}$

$$M_{2,\alpha}(k_t) = (-1)^\alpha \sum_{\beta=1}^{p} (E_{2,\beta}(k_t))^\alpha, \quad M_{n-2,\alpha}(k_t) = \sum_{\beta=1}^{p} (E_{n-2,\beta}(k_t))^\alpha .$$

From this we simply obtain

$$Tr(\mathbf{U}^{\alpha-1}\mathbf{V}) = Q_\alpha, \qquad (20)$$

for

$$Q_\alpha = \tfrac{1}{2} |M_{n-2,\alpha}(k_t) - $$
$$- M_{2,\alpha}(k_t), k_t^{\alpha-3}, \ldots, k_t^{\alpha-1-2[\alpha/2-1/2]}| / \alpha \, | k_t^{\alpha-1}, k_t^{\alpha-3}, \ldots, k^{\alpha-1-2[\alpha/2-1/2]} | ,$$

where $\alpha = 1,2, \ldots, \binom{n}{2}$ and $t = 1,2, \ldots, [(\alpha - 1)/2]$. From the assumption *a)* of theorem *3* it follows that the determinant in the denominator is nonzero. With regard to the form of matrices $\mathbf{H}_2(k_t)$ and $\mathbf{H}_{n-2}(k_t)$ it follows from *(20)* that

$$\sum_{\mathbf{x}\in D^n, n(\mathbf{x})=2}^{n} (\mu(\mathbf{x}))^{\alpha-1} \, \hat{J}(\mathbf{x}) = Q_\alpha, \qquad (21)$$

where

$$\mu(\mathbf{x}) = \tfrac{1}{2} \sum_{j=1} v_j x_j, \quad \hat{J}(\mathbf{x}) = \tfrac{1}{4} \sum_{1\leq i<j\leq n} J_{ij} x_i x_j . \qquad (22), (23)$$

The determinant of the system *(21)* is different from zero if and only if $(\mathbf{x} \in D^n, \mathbf{y} \in D^n, \mathbf{x} \neq \mathbf{y}, n(\mathbf{x}) = n(\mathbf{y}) = 2) \Rightarrow \mu(\mathbf{x}) \neq \mu(\mathbf{y})$, which is identical with the assumption *b)* of theorem *3*. Hence

$$\hat{J}(\mathbf{x}_k) = |(\mu(\mathbf{x}_1))^\alpha, \ldots, (\mu(\mathbf{x}_{k-1}))^\alpha, Q_\alpha, (\mu(\mathbf{x}_{k+1}))^\alpha, \ldots, (\mu(\mathbf{x}_t))^\alpha| :$$
$$: |(\mu(\mathbf{x}_1))^\alpha, (\mu(\mathbf{x}_2))^\alpha, \ldots, (\mu(\mathbf{x}_t))^\alpha| ,$$

where $t = \binom{n}{2}$, the row index $\alpha = 1,2,\ldots, t$ and $\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_t$ is an arbitrary ordering of the set $\{\boldsymbol{x} \in D^n \mid n(\boldsymbol{x}) = 2\}$. To complete the proof, it is sufficient to show that Eqs (*23*) are uniquely solvable with respect to J_{ij}. Rows of the matrix of this system are indexed by vectors $\boldsymbol{x}(\boldsymbol{x} \in D^n,\ n(\boldsymbol{x}) = 2)$, each of them being uniquely defined by a pair of such indexes i', j' for which the corresponding coordinates of the vector $\boldsymbol{x}$ are equal to $+1$. Columns of this matrix correspond to pairs (i, j) in J_{ij}. We now arrange the rows and columns of the matrix of the system (*23*) arbitrarily so that the sequence of the pairs (i, j) becomes the same as the sequence of the pairs (i', j'). We denote this new matrix as $\boldsymbol{A}$, the vector of the solution J_{ij} as $\boldsymbol{J}$, and the vector of the right sides $\hat{\boldsymbol{J}}(\boldsymbol{x})$ as $\hat{\boldsymbol{J}}$, and rewrite the system (*23*) in the form

$$\boldsymbol{A}\boldsymbol{J} = 4\hat{\boldsymbol{J}}\,. \tag{23a}$$

The following auxiliary assertion implies that the latter system is uniquely solvable and also implies the form of the solution, which completes the proof.

Lemma 2: Let $n > 4$. Then $\boldsymbol{A}$ is regular and

$$\boldsymbol{A}^{-1} = \alpha\boldsymbol{A} + \beta\boldsymbol{1} + \gamma\boldsymbol{I}\,, \tag{24}$$

where $\boldsymbol{1}$ denotes matrix of the type $\binom{n}{2} \times \binom{n}{2}$ consisting only of unities, $\boldsymbol{I}$ unit matrix of the same type and $\alpha = 1/8(n - 4)$, $\beta = (5 - n)\ (n - 8)/8(n - 4)\ (n^2 - 9n + 16)$, $\gamma = (n - 6)/4(n - 4)$. (For a proof of this lemma see Appendix.)

APPENDIX

Proof of lemma 1: Without loss of generality, it can be assumed that the rows and columns of matrices $\boldsymbol{C}$ and $\boldsymbol{D}$ are ordered according to the following scheme:

$$(-1, -1, \ \ 1, 1)\,,\ \ (-1, \ \ 1, -1, \ \ 1)\,,\ \ (-1, 1, \ \ 1, -1)\,,$$
$$(\ \ 1, -1, -1, 1)\,,\ \ (\ \ 1, -1, \ \ 1, -1)\,,\ \ (\ \ 1, 1, -1, -1)\,.$$

It can be easily verified that in such a case $\boldsymbol{C} = -\hat{\boldsymbol{I}}_6\boldsymbol{C}\hat{\boldsymbol{I}}_6$ and $\boldsymbol{D} = \hat{\boldsymbol{I}}_6\boldsymbol{D}\hat{\boldsymbol{I}}_6$, where $\hat{\boldsymbol{I}}_6$ denotes a 6×6 matrix whose elements on the subordinate diagonal are equal to 1 and others are zero. (The transformation $\hat{\boldsymbol{I}}_6\boldsymbol{X}\hat{\boldsymbol{I}}_6$ converts the 6×6 matrix $\boldsymbol{X}$ into $\boldsymbol{X}'$ differing from $\boldsymbol{X}$ by an inverse order of rows and columns.) Since $(\hat{\boldsymbol{I}}_6)^2$ is a unit 6×6 matrix and r is odd, we obtain

$$Tr(\boldsymbol{C}^r\boldsymbol{D}^s) = Tr(-(\hat{\boldsymbol{I}}_6\boldsymbol{C}\hat{\boldsymbol{I}}_6)^r\,(\hat{\boldsymbol{I}}_6\boldsymbol{D}\hat{\boldsymbol{I}}_6)^s) = -\,Tr(\hat{\boldsymbol{I}}_6\boldsymbol{C}^r\boldsymbol{D}^s\hat{\boldsymbol{I}}_6) = -\,Tr(\boldsymbol{C}^r\boldsymbol{D}^s)\,,$$

whence follows $Tr(\boldsymbol{C}^r\boldsymbol{D}^s) = 0$. The proof is accomplished.

Proof of lemma 2: The columns of the matrix $\mathbf{A}$ are numbered with ordered pairs (i, j), $1 \leqq i < j \leqq n$. To simplify the proof, we shall consider (i, j) as a two-element subset $\{i, j\}$ of the set $\{1,2, \ldots, n\}$, where $i \neq j$; this allows us to take advantage of the symmetry $\{i, j\} = \{j, i\}$. In a similar way, we shall number the rows of the matrix $\mathbf{A}$ with all two-element subsets $\{i', j'\}$ of the set $\{1,2, \ldots, n\}$. Thus, $\mathbf{A}(\{i', j'\}, \{i, j\})$ denotes an element of the row $\{i', j'\}$ and column $\{i, j\}$ of the matrix $\mathbf{A}$ (analogously also for other matrices occurring below). It is apparent from the form of the system *(23)* that $\mathbf{A}(\{i', j'\}, \{i, j\}) = x_i x_j$, where the vector $\mathbf{X} \in D^n$ has i'th and j'th components equal to 1. Now the elements of the matrices $\mathbf{A}$, $\mathbf{1A}$ and $\mathbf{A}^2$ will be determined.

Elements of the matrix $\mathbf{A}$: *a*) If $\{i', j'\} = \{i, j\}$, then $\mathbf{A}(\{i, j\}, \{i, j\}) = x_i x_j = (+1)(+1) = 1$. *b*) If $\{i', j'\} \cap \{i, j\} = \emptyset$, then $\mathbf{A}(\{i', j'\}, \{i, j\}) = x_i x_j = (-1) . (-1) = 1$. *c*) If $\{i', j'\} \cap \{i, j\}$ is a one-element set then $\mathbf{A}(\{i', j'\}, \{i, j\}) = x_i x_j = (+1)(-1)$ or $(-1)(+1) = -1$. Hence, $\mathbf{A}$ is symmetrical.

Elements of the matrix $\mathbf{1A}$: $(\mathbf{1A})(\{i', j'\}, \{i, j\}) = \sum_{\{r,s\}} \mathbf{1A}(\{r, s\}, \{i, j\}) = -(\binom{n-2}{2} + 1)(+1) + (\binom{n}{2} - \binom{n-2}{2} - 1(-1) = 2 + 2\binom{n-2}{2} - \binom{n}{2}$, where the sum is taken over all $\{r, s\} \subset \{1,2, \ldots, n\}$, $r \neq s$. Hence, $\mathbf{1A} = (2 + 2\binom{n-2}{2} - \binom{n}{2})\mathbf{1}$.

Elements of the matrix $\mathbf{A}^2$: Since the matrix $\mathbf{A}$ is symmetrical, $\mathbf{A}^2 = \tilde{\mathbf{A}}\mathbf{A}$ and hence $(\mathbf{A}^2)(\{i', j'\}, \{i, j\}) = (\tilde{\mathbf{A}}\mathbf{A})(\{i', j'\}, \{i, j\}) = \sum_{x \in D^n, n(x)=2} x_{i'} x_{j'} x_i x_j$.

We shall distinguish three cases: *a*) $\{i', j'\} = \{i, j\}$, *b*) $\{i', j'\} \cap \{i, j\} = \emptyset$, *c*) $\emptyset \neq \{i', j'\} \cap \{i, j\} \neq \{i, j\}$. In case (*a*) we obtain $\mathbf{A}^2(\{i', j'\}, \{i, j\}) = \sum_{x \in D^n, n(x)=2} 1 = \binom{n}{2}$. In case (*b*) we have $\mathbf{A}^2(\{i', j'\}, \{i, j\}) = \sum_{x \in D^n, n(x)=2} x_{i'} x_{j'} x_i x_j = 4(n-4)(-1) + (\binom{n}{2} - 4(n-4)(+1) = \binom{n}{2} - 8(n-4)$. In case *c*) we set $\{k, l\} = \{i', j', i, j\} - \{i', j'\} \cap \{i, j\}$. Then $\mathbf{A}^2(\{i', j'\}, \{i, j\}) = \sum_{x \in D^n, n(x)=2} x_{i'} x_{j'} x_i x_j = \sum_{x \in D^n, n(x)=2} x_k x_l = 2(n-2)(-1) + (\binom{n}{2} - 2(n-2))(+1) = \binom{n}{2} - 4(n-2)$.

To accomplish the proof, it remains to show the existence of numbers α, β and γ satisfying the matrix equation $(\alpha\mathbf{A} + \beta\mathbf{1} + \gamma\mathbf{I})\,\mathbf{A} = \mathbf{I}$, i.e. $\alpha\mathbf{A}^2 + \beta(\mathbf{1A}) + \gamma\mathbf{A} = \mathbf{I}$. It follows from the preceding that the latter equation is equivalent to the following system of equations for α, β and γ:

$$\binom{n}{2}\alpha + \left(2 + 2\binom{n-2}{2} - \binom{n}{2}\right)\beta + \gamma = 1\,,$$

$$\left(\binom{n}{2} - 8(n-4)\right)\alpha + \left(2 + 2\binom{n-2}{2} - \binom{n}{2}\right)\beta + \gamma = 0\,,$$

$$\left(\binom{n}{2} - 4(n-2)\right)\alpha + \left(2 + 2\binom{n-2}{2} - \binom{n}{2}\right)\beta - \gamma = 0\,.$$

This system has a unique solution (α, β, γ) given by Eqs (*24*), which completes the proof.

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