A testing procedure for determining the chemical rank of spectroscopic absorption matrices - a heuristic approach

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Abstract

We will discus a method for determining location shifts in normally distributed matrices for use with apsorption matrices. A testing methodology will be produced and argued for.

1 Determining chemical rank

In spectrometrical investigations the absorption of light of different wavelengths are measured. The laws of chemistry gives that the rank of the matrix of absorption is equal to the number of photocromatic species in the sample. If we where analysing a pure sample of the chemical of interest and the measurement apparatus would be without measurment errors this would be a true. In reallity no solutions are pure and no apparatus is without errors and hence the rank of the matrix will differ from the chemical rank. This problem is closely relatad to the problem of determining the number of components to use in Principal Component Regression (PCR). The law that controls the absorption i.e. Beer's law, makes it natrual to use factorisation methods.

When using sub-space methods, i.e. methods solving the problem on a smaller space than the original space, one needs a method to estimate the size of the sub-space. In many applications the predictive properties are the propperties that is wished to be optimal. In many methods to asses

a stop criteria different estimates of the Mean Squared Error of Prediction (MSEP) is used. The most common way of of estimating MSEP is through cross validation, see Denham (2000) for an overview. It is known that cross validation might give incorrect estimates of the minimum of the MSEP, see Adolfsson (1999) or Faber (2001).

In the case of PCR there is a stepdown test that can be used. This test uses the fact that the eigenvalues and eigenvectors used is given by a deterministic matrix which used in a correct way will produce a t-test. The same method has been used for PLS but here the basevectors for the regressionspace is not deterministicly choosen so the theory does not hold, see Faber (2001). It must be recognised that when testing in such situations as this, the concept of multiple inference must play a central role. In many investigations a large number of hypothesis are tested and it is plausible that many rejections might occur only by chance if the inference is based on individual tests.

One should also be aware (as a statistician) that the research communities that use these method are more result than theory oriented. Statisticians rather want to test in a fashion that can be understod while reasearchers tend to want a good answer. In deciding for a method to asses the regression space one must remember that in solving a collinear regression problem the main idea is not to include all theoretical effects but rather to include all the effects that are big enough to stabilise the problem. Including to small effects will give such increase in variance that the solution becomes useless in a practical sense. A test should hence be constructed to be powerfull against alternatives where the effect is as large as the level of variance. The lack of such method is due to the complexness of the distributions arising in these problems. An approach that becomes more and more tractable with the growing speed of computers is to use a statistic with the correct theoretical properties and that can be simulated. It is my belief that this is the necessary way of moving this field forward.

One should be aware of the problem of estimating the chemical rank of the matrix and that of estimating the rules that governs the concentrations in a spectrometrical trial. The chemical rank gives the number of photocromatically active species in the trial. This is not necessarily the same as the number of photocromatilly active *interesting* species.

2 Intuitive background of the test procedure

We start with some well known facts from elemetary linear algebra. Let A be a $n \times n$ real matrix s.t. $A' = A > 0$. We consider the function $f(\mathbf{x}) : \mathbb{R}^{\mathbf{n}\times\mathbf{n}} \to \mathbb{R}$ where $f(\mathbf{x}) = \mathbf{x}'A\mathbf{x}$. If wee set $n = 2$ and plot the function for $|\mathbf{x}| = 1$ we get an ellipsoid of the type shown in figure 1. Since $A > 0$

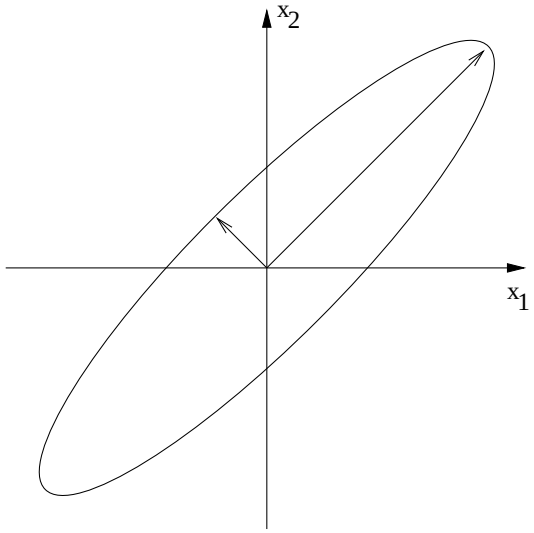

Figure 1: A plot of $f(\mathbf{x})$

we know that the eigenvalues $\lambda_1 > \lambda_2$ of A are positive. The length of the largest of the principal axis of the ellipsoid is given by λ_1 and the shortest principal axis by λ_2. The direction of the axis correspond to the eigenvectors of the matrix. A measure of "the stretch" of the ellipsoid is given by λ_1/λ_2 which, in numerical literature, is reffered to as the condition number of the matrix A. The same thing obviously hold for $n > 2$ but plotting becomes impossble (at least for $n > 3$). In the case $n > 2$ we let $\lambda_1 > \ldots > \lambda_n > 0$ be the eigenvalues of A and the condition number is now given by λ_1/λ_n. A good thing with the condition number and similar measures is that of the matrix is stretched out by a scalar, i.e. $A = \alpha B$, the condition number of A and B are the same.

The time has now come to start with stochastic matrixes. Let us assume that $W \sim W_p(\mathbf{0}, I_p\sigma^2, n)$, $n > p$. A matrix with this Wishart distribution will a.s. be positively definite and its eigenvalues are a.s. distinct. The

distribution of the eigenvalues is known but rather complicated to use for direct calculations. We will try to avoid going into detail of the distribution but rather se what we can do in general. One well known fact of the Wishart distribution is that if $W_1 \sim W_p(\mathbf{0}, I_p, n)$ then $\sigma^2 W_1 \stackrel{\mathcal{D}}{=} W$. This gives that if λ_i is a (stochastic) eigenvalue of W_1 then $\sigma^2\lambda_i$ is a (stochastic) eigenvalue of W. We now know that any statistic on the form $\frac{\lambda_1}{\lambda_i}$ does not depend on σ. To make the qoutient more stable we study

$$R = \frac{\lambda_1}{\sum_{i=n-r}^{n} \lambda_i} \tag{1}$$

which also is independent of σ. This is also a measure of the skewness of the ellipsoid but more stabilised than using just λ_n in the denominator. The only thing that we know about this statistic is that it is independent of σ but we also now how to generate a sample of stocastic variable with this distribution in a computer.

3 Theoretical properties of the test procedure

We will construct our test procedur using the statistic defined in (1). As mentioned before this statistica gives a measure of how skew the level curves of the quadratic form given by the matrix is. The statistic gives a bound for the maximal natrual variation and the idea is to see what directions exceeds this natrual variation bound. This problem is in chemometrics known as the problem of determining the chemical rank of a matrix. The test procedure will not be proven to work with the correct multipel level of significans but will be made likely to work. The problem with stating a formal proof of the level of significans is due to the problem of making statements about the singular values of the sum of two matrices. I will however give a intuitive explanation of why this should work. The first assumptions that is made is that the matrix of measurements is actually a sum of two matrices. Let Y be a $n \times p$ matrix where each row comes from independent $N_n(\mathbf{0}, \sigma^2 I_p)$ distributions. Let M be a deterministric matrix of size $n \times p$. Let the rank of M be r. Let the matrix of measurements $X = M + Y$. The problem is to find r given X. For computional convenience I choose to work with the singular values of X. There is no *theoretical* difference since the singular values of X is mearly the square root of the eigenvalues of $X'X$ but practically we save a matrix multiplication in computing.

As mentioned earlier the correctness of the testing procedure is hard to make rigorous. However, there are some reasons why the method should work. There is a version of the Courant-Fisher theorem for singular values that will come in handy to understand how the method works.

Theorem 1 *Let A be a $n \times m$ matrix, let $\sigma_1(A) \geq \sigma_2(A) \geq \ldots$ be the ordered singular values of A, and let k be a given integer with $1 \leq k \leq \min\{m, n\}$. Then*

$$\sigma_k(A) = \min_{w_1,\ldots,w_{k-1} \in \mathbb{C}^n} \max_{\substack{x \in \mathbb{C}^n \\ \|x\|_2 = 1 \\ x \perp w_1,\ldots,w_{k-1}}} \|Ax\|_2 \tag{2}$$

$$= \max_{w_1,\ldots,w_{n-k} \in \mathbb{C}^n} \min_{\substack{x \in \mathbb{C}^n \\ \|x\|_2 = 1 \\ x \perp w_1,\ldots,w_{n-k}}} \|Ax\|_2 \tag{3}$$

$$= \min_{\substack{S \subset \mathbb{C}^n \\ \dim\{S\}=k}} \max_{\substack{x \in S \\ \|x\|_2 = 1}} \|Ax\|_2 \tag{4}$$

$$= \max_{\substack{S \subset \mathbb{C}^n \\ \dim\{S\}=k}} \min_{\substack{x \in S \\ \|x\|_2 = 1}} \|Ax\|_2 \tag{5}$$

From this we see that, if $\sigma_1(A)$ is the biggest singular value, (2) above reduces to $\sigma_1(A) = \max_{||x||_2=1} ||Ax||_2$. If we to the matrix A add a "dominant direction", which corresponds to a true (large) effect then $\sigma_1(A)$ will increase. If this dominant direction is unequal to the direction x used for calculating $\sigma_1(A)$ any succeeding $\tilde{\sigma}_k(A), \quad k \neq 1$ will be larger than the original $\sigma_k(A)$! This is a key element in the reasoning for multipel inference. We will now study this phenomena in greater detail. Let us assume that Y is defined as earlier. The product YY'/n is a estimation of $\sigma^2 I_p$. The rows of Y will not show any systematic variations since they estimate zero i.e. $\frac{1}{n}\sum_{i=1}^{n} Y_{ij} \to 0$ a.s.. If we now add a matrix $M = (m_1', m_2', \ldots, m_n')'$ to Y where the rows in M have the structure $m_i = \alpha m_j$, $\alpha > 0$ for some $i \neq j$ the column sums no longer estimate zero (or at least need not). This assumption might seem strange but is a higly relevant assumption when dealing with spectroscopic data. The assumption is meerly stating that Beer's law is walid which is a assumption that is made in most (not to say all) spectroscopic investigations. If the rank of M is $r < \min(n, p)$ this will tend to make a r-dimensional space have a larger spread than the other directions. This will happen since,

if we once again look at $X'X$, the other dimensions meerly estimates a ball with radius σ^2. This means that the matrix M only affects a r dimensional space and leaves the rest of the dimensions unchanged. This will change the directions of the largest singular values if the size of the m_i:s is large enough compared with σ^2. Since the directions for the large singular values are changed the optimisation in theorem 1 for the smaller singular values that does not contain any true effects will be in other directions which now might include the larger directions in Y and hence the singular values will be larger.

Theorem 2 (Multipel test procedure) *Let $Y \sim N_n(\mathbf{0}, \sigma^2 I_p)$ with $n < p$ and $M \in \mathbb{R}^{n \times p}$ be such that the assumptions above are fulfilled. Let $\sigma_1(X) \geq \ldots \geq \sigma_p(X) > 0$ be the singular values of $X = Y + M$. Then testing the hypothesis $H_{0i} : \sigma_i(X) = \sigma_i(Y)$ against $H_{1i} : \sigma_i(X) = \sigma_i(\tilde{Y}) + \mu(M)$ by the procedure reject H_{0i} if $\sigma_i(X)/Q_X > e_\alpha$, where $Q_X = \sum_{i=n}^{n-k} \sigma_i(X)$ and e_α is chosen such that*

$$\mathbb{P}\left\{\frac{\sigma_1(Y)}{Q_Y} > e_\alpha\right\} = \alpha,$$

maintains the multipel level of significans α.

Proof: By the definition of e_α the overall conjunction trivially has the correct level of significans. So let us now assume that some H_{1i} is true. From the assumptions above we have that $Q_Y \leq Q_X$. Let $\tilde{Y}$ be a s.v. such that $\sigma_i(X) = \sigma_i(\tilde{Y}) + \sigma_i(M)$. Let us now study the artificial test based on $\tilde{Y}$. This test satisfy

$$\begin{aligned}
\mathbb{P}\left\{\frac{\sigma_i(\tilde{Y})}{Q_{\tilde{Y}}} \leq e_\alpha \forall i\right\} &= 1 - \mathbb{P}\left\{\exists i : \frac{\sigma_i(\tilde{Y})}{Q_{\tilde{Y}}} > e_\alpha\right\} \\
&= 1 - \mathbb{P}\left\{\frac{\max_i \sigma_i(\tilde{Y})}{Q_{\tilde{Y}}} > e_\alpha\right\} \\
&\geq 1 - \mathbb{P}\left\{\frac{\sigma_1(Y)}{Q_Y} > e_\alpha\right\} = 1 - \alpha.
\end{aligned}$$

By construction we have that $\sigma_i(X)/Q_X \leq \sigma_i(\tilde{Y})/Q_{\tilde{Y}}$ if H_{0i} is true and hence the real testing procedur will give no more rejections than the artificial one. **Q.E.D.**

4 Simulations results

Simulations where used to examine the performance of the testing procedure. The following algorithm was used:

1. Generate $B_1', \ldots B_r' \sim N_p(0,1)$ (base vectors) and $U_1, \ldots U_r \sim U_n(0,1)$. Set $M = U'B$.
2. FOR I=1 TO number of samples DO
   (a) SET $E = N_n(0, \sigma^2 I_p)$ AND $X = M + E$.
   (b) CALCULATE data=SVD(X).
   (c) SET $S = \sum_{i=n-k+1}^{n} \lambda_i$ AND STAT= $\frac{\lambda_1}{S}$.
   (d) DO TEST.
   (e) SAVE number of rejections.
3. calculate statistics.

This means that we will have a different deterministic matrix each time we run the program. In the simulations $n = 47$, $p = 28$ and $k = 14$ where used. When r was set to zero the rejection rate was α (in the simulations set to 10%). With $r = 1$ the false rejection rate was meerly 1% and when $r = 2$ the false rejection rate was 0.1%. For $r \geq 3$ no false rejections where made. The power is good when the true rank of the matrix M is small compared to the total number of singular values. This can be explained with use of theorem 1. The true effects move the space for the minimisation of the smallest singular values and hence the smallest singular values will be to large, thus making the testing procedure conservative.

We now set $n = 50$, $p = 40$, $k = 25$, $r = 10$, and $\sigma = 0.5$. The mean number of the estimated rank is now 8.65. A plot of the 28 largest normed singular values and the rejection boundary for $\alpha = 0.10$ of one test realisation can be found in figur 2. Note that the plotted normed singular values have no distinct bend even thou it contains skifts. In this case it would difficult to estimate the dimension by inspection.

5 An example

The following example is taken from Hjorth (1994) and consern paper industri. A complete description of the dataset can be found on pages 74-76

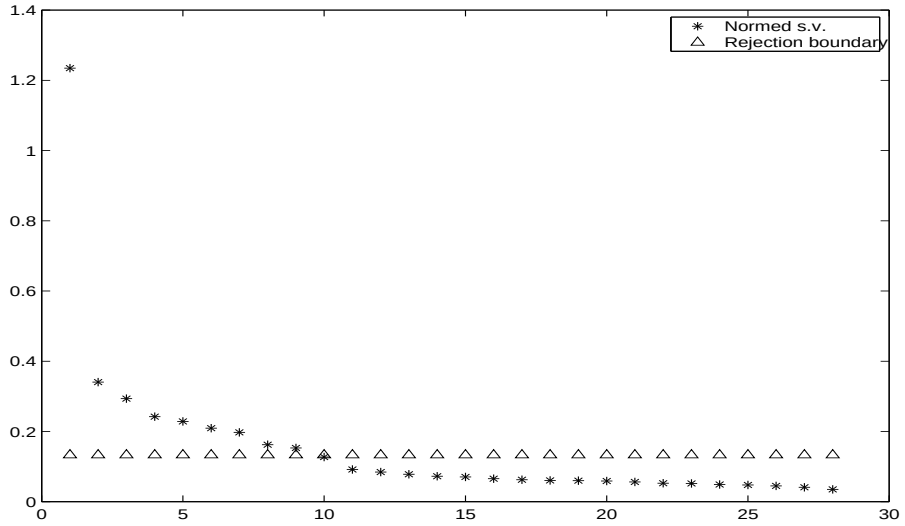

Figure 2: Plot of statistic and boundary for simulated data

in Hjorth (1994). The data is 48 observations on a 28-dimensional vector of variates. The testing procedure using $\alpha = 0.10$ and $r = 14$ gives that the estimated true rank of the data is 8. A plot of the statistics and the boundary can be found in figur 3

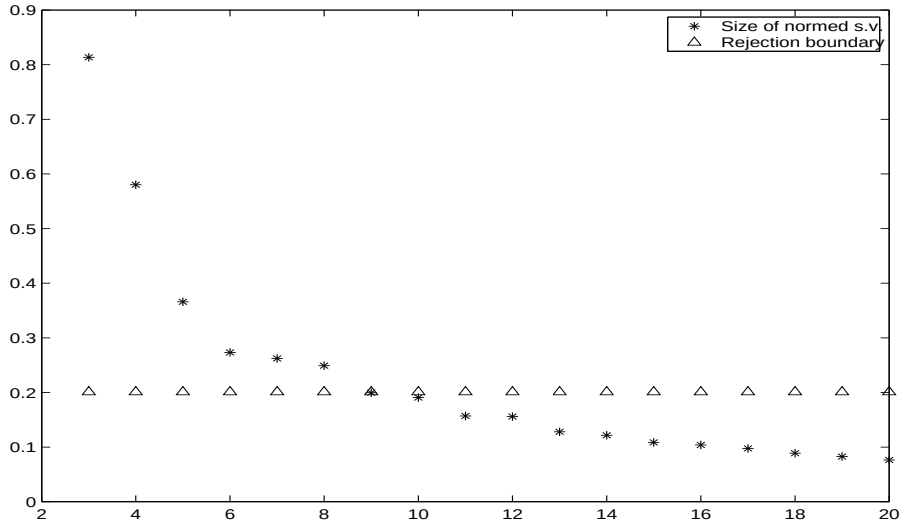

Figure 3: Plot of statistic and boundary for paper data

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