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Supporting information for article:

X-ray constrained Spin-Coupled Technique: Theoretical Details and Further Assessment of the Method

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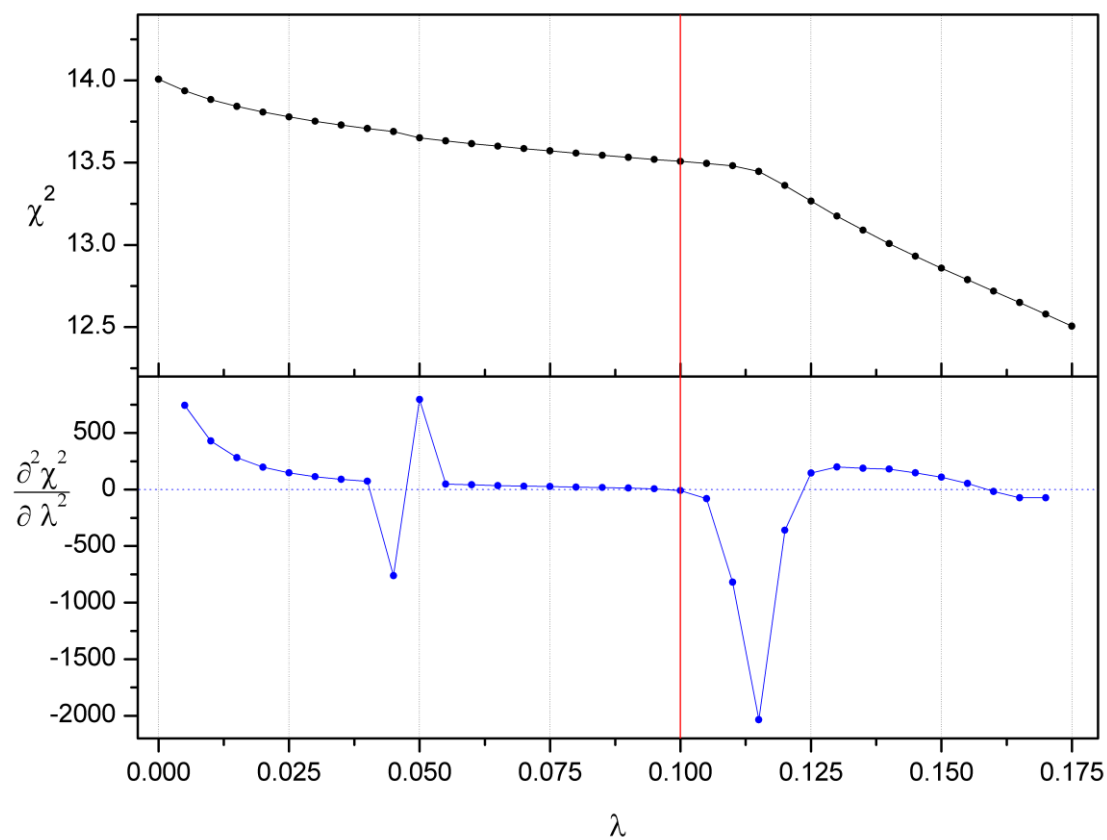
Figure S1 χ^2 and $\partial^2\chi^2/\partial\lambda^2$ in function of the external multiplier λ for the XCSC.0 calculation with basis-set 6-31G. The vertical red line indicates the λ value at which the XCSC.0 calculation was halted.

Figure S2 χ^2 and $\partial^2\chi^2/\partial\lambda^2$ in function of the external multiplier λ for the XCSC.0 calculation with basis-set 6-311G. The vertical red line indicates the λ value at which the XCSC.0 calculation was halted.
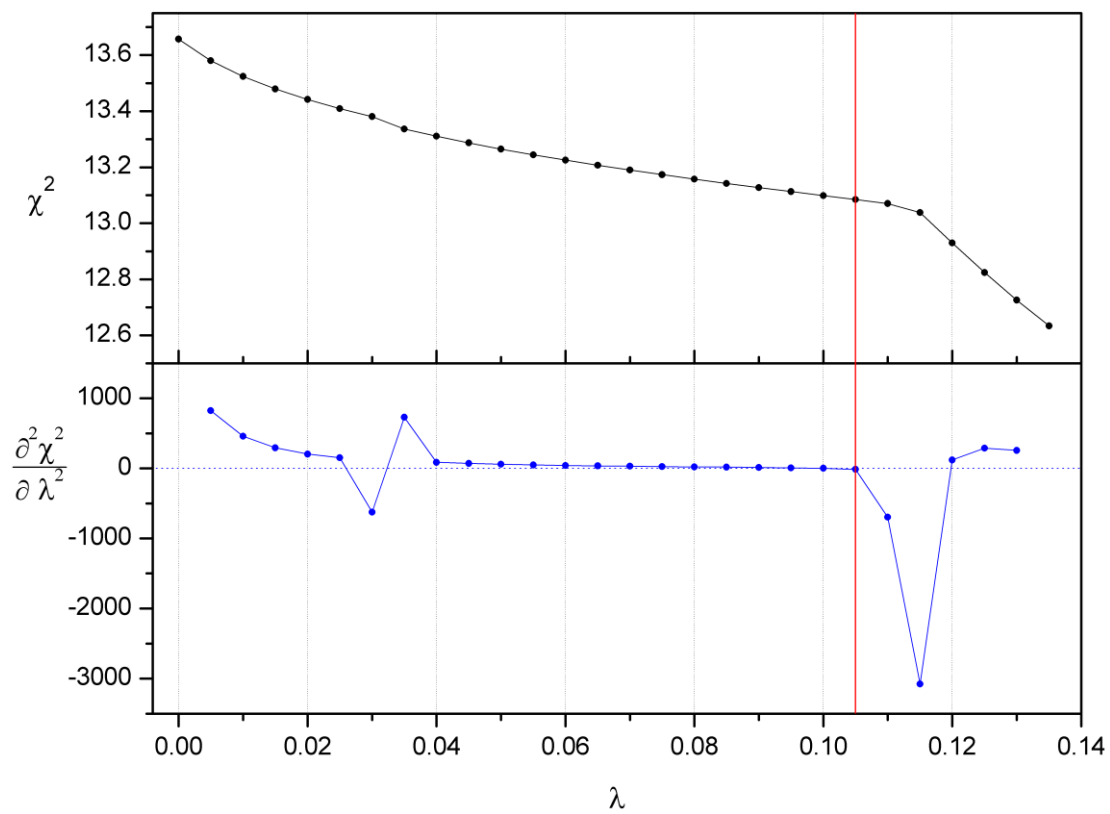
Figure S3 χ^2 and $\partial^2\chi^2/\partial\lambda^2$ in function of the external multiplier λ for the XCSC.0 calculation with basis-set 6-31G(d). The vertical red line indicates the λ value at which the XCSC.0 calculation was halted.

Figure S4 χ^2 and $\partial^2\chi^2/\partial\lambda^2$ in function of the external multiplier λ for the XCSC.0 calculation with basis-set 6-311G(d). The vertical red line indicates the λ value at which the XCSC.0 calculation was halted.
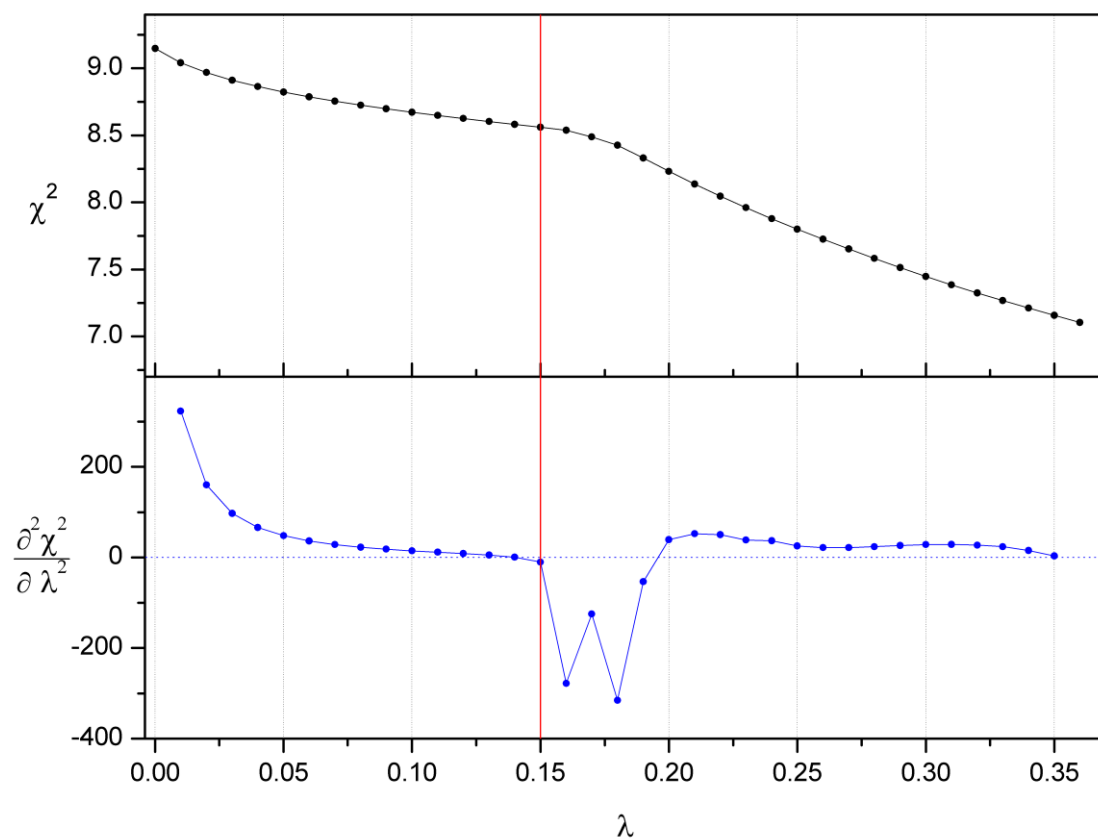
Figure S5 χ^2 and $\partial^2\chi^2/\partial\lambda^2$ in function of the external multiplier λ for the XCSC.1 calculation with basis-set 6-31G. The vertical red line indicates the λ value at which the XCSC.1 calculation was halted.
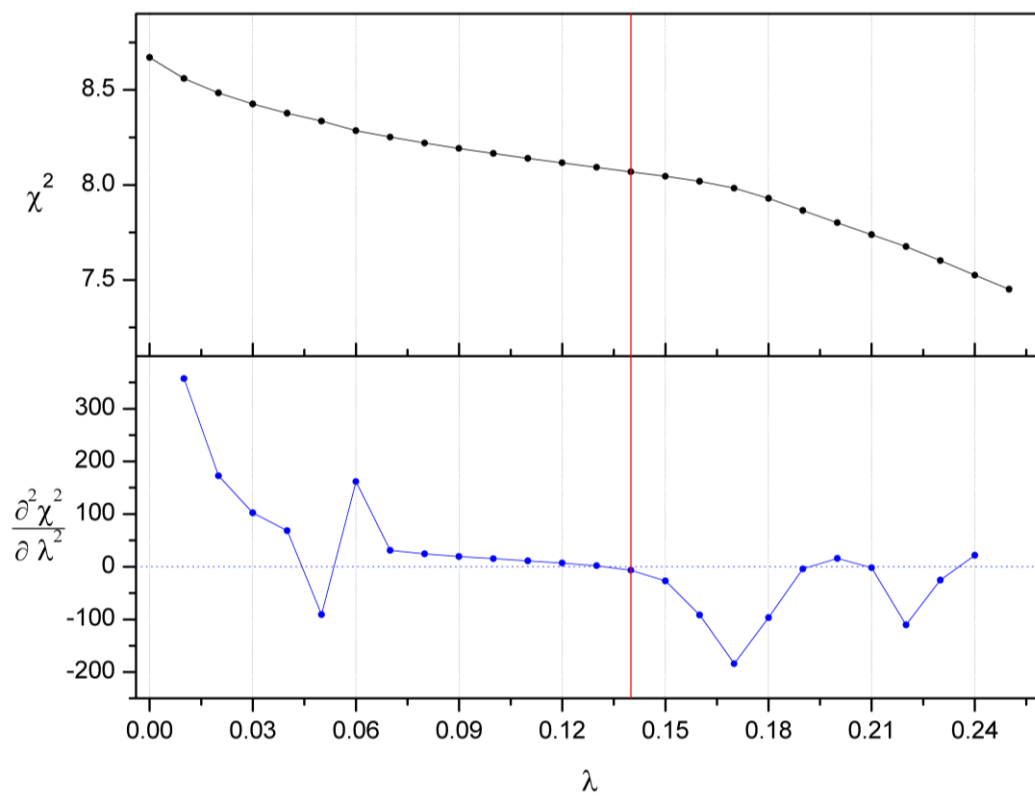
Figure S6 χ^2 and $\partial^2\chi^2/\partial\lambda^2$ in function of the external multiplier λ for the XCSC.1 calculation with basis-set 6-311G. The vertical red line indicates the λ value at which the XCSC.1 calculation was halted.

Figure S7 χ^2 and $\partial^2\chi^2/\partial\lambda^2$ in function of the external multiplier λ for the XCSC.1 calculation with basis-set 6-31G(d). The vertical red line indicates the λ value at which the XCSC.1 calculation was halted.
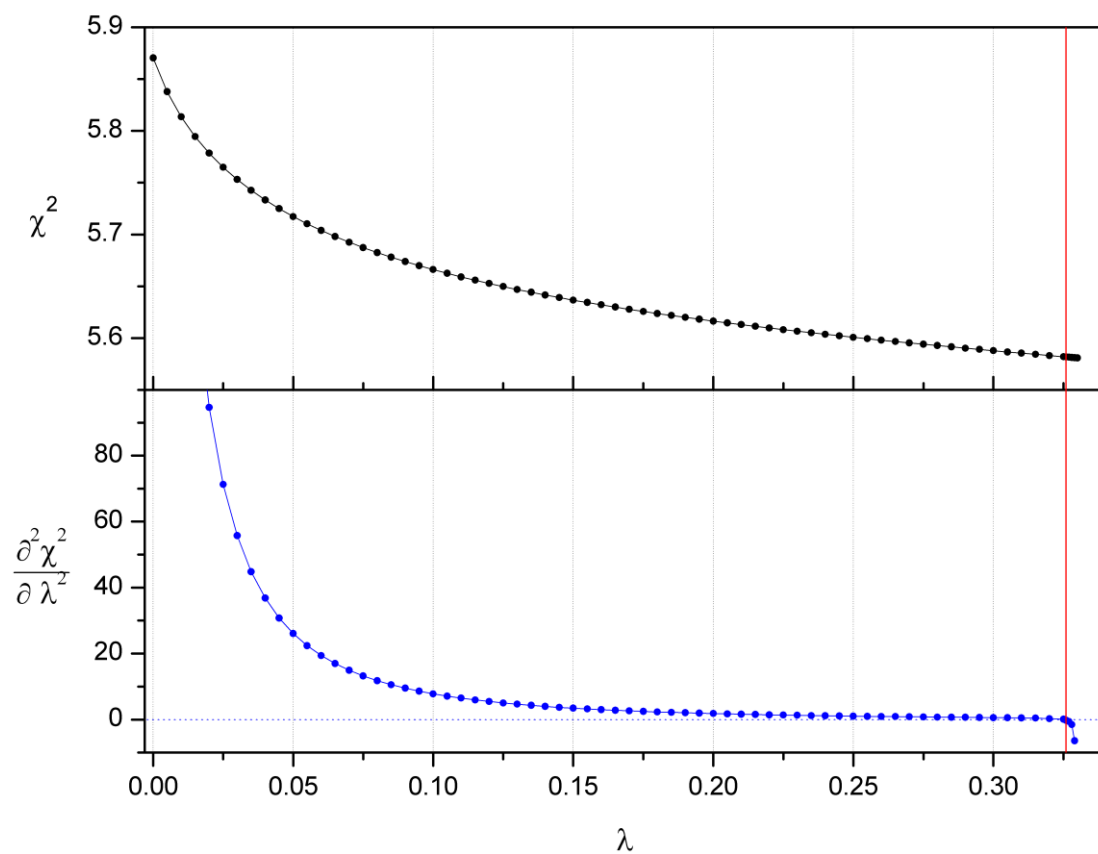
Figure S8 χ^2 and $\partial^2\chi^2/\partial\lambda^2$ in function of the external multiplier λ for the XCSC.1 calculation with basis-set 6-311G(d). The vertical red line indicates the λ value at which the XCSC.1 calculation was halted.
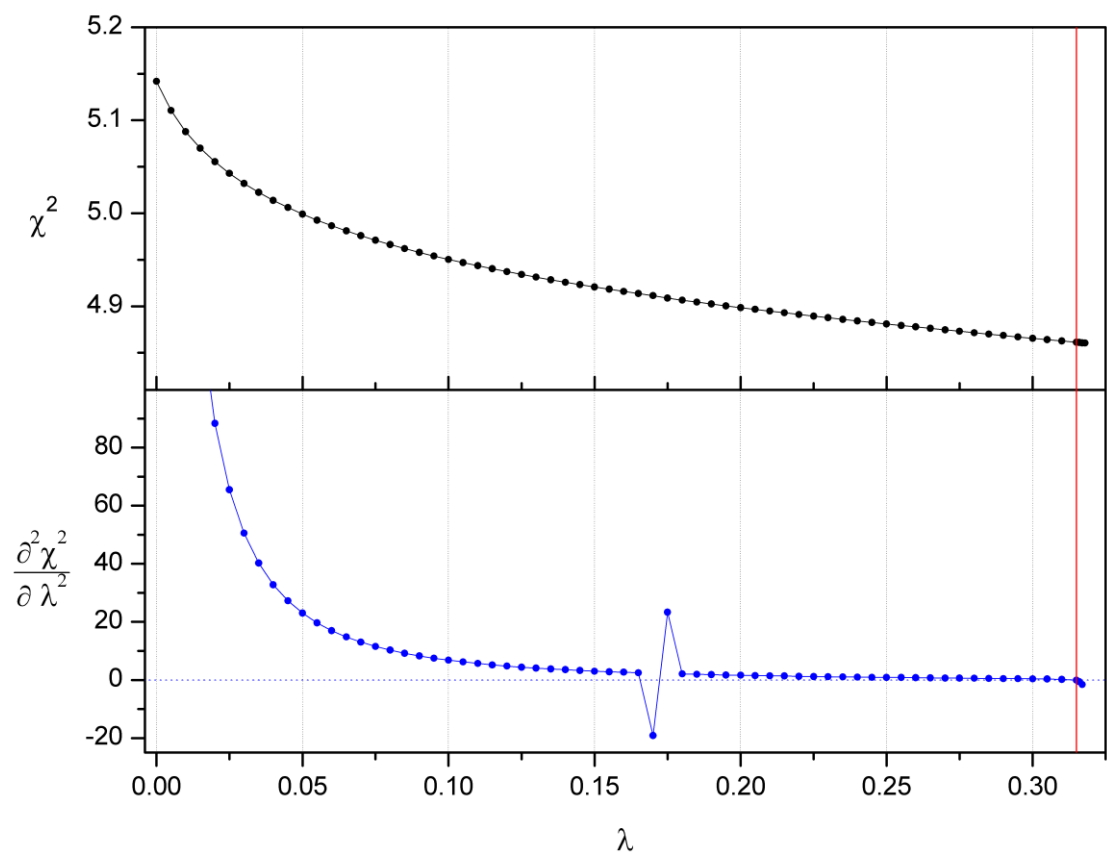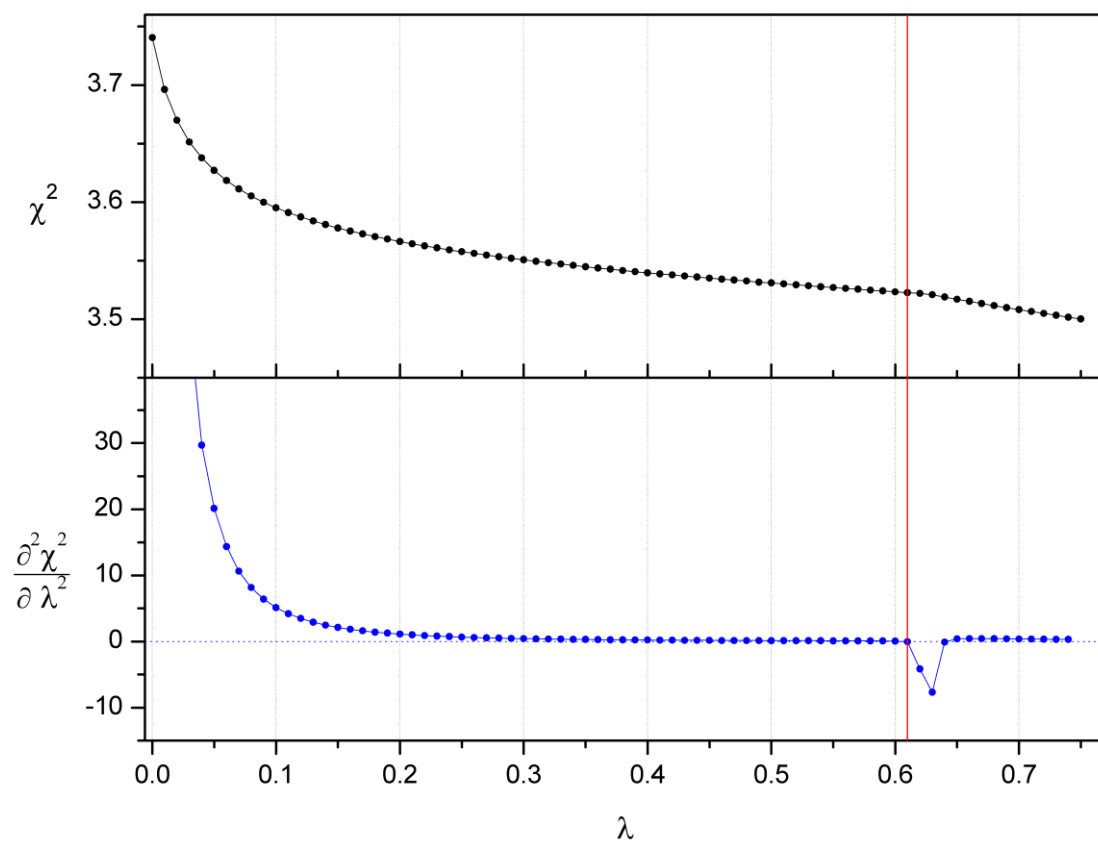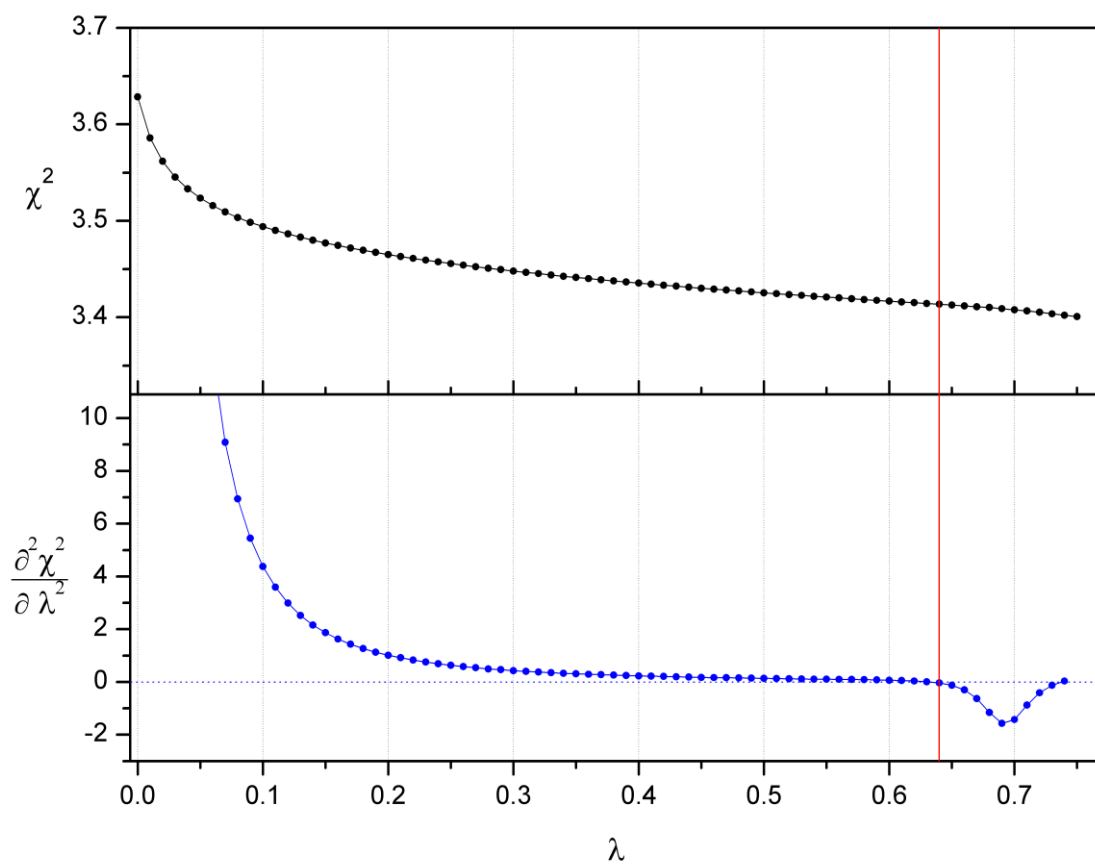
Theoretical details about the Walker-Mezey similarity index

The Walker-Mezey similarity index $L(\rho_x, \rho_y, a, a')$ is defined by the following equation:

$$L(\rho_x, \rho_x, a, a') = 100 \; \frac{L^*(\rho_x, \rho_y, a, a') + L^*(\rho_y, \rho_x, a, a')}{2} \qquad (S1)$$

where

$$L^*(\rho_x, \rho_y, a, a') = 1 - \left[\sum_{r \in S(\rho_x, a, a')} \frac{|\rho_x(r) - \rho_y(r)|}{max\left(\rho_x(r), \rho_y(r)\right)} \right] \Big/ n(S(\rho_x, a, a')) \quad (S2)$$

and

$$L^*(\rho_y, \rho_x, a, a') = 1 - \left[\sum_{r \in S(\rho_y, a, a')} \frac{|\rho_x(r) - \rho_y(r)|}{max\left(\rho_x(r), \rho_y(r)\right)} \right] \Big/ n(S(\rho_y, a, a')) \quad (S3)$$

with

$$S(\rho_x, a, a') = \{r : a \leq \rho_x(r) \leq a'\} \qquad (S4)$$

and

$$S(\rho_y, a, a') = \{r : a \leq \rho_y(r) \leq a'\} \qquad (S5)$$

$S(\rho_x, a, a')$ and $S(\rho_y, a, a')$ are the "density shells" inside which the point-by-point comparisons of the electron densities are performed and can be considered as three-dimensional spaces bound by the two isosurfaces a and a' of the electron densities ρ_x and ρ_y, respectively. $n(S(\rho_x, a, a'))$ and $n(S(\rho_y, a, a'))$ in equations (S2) and (S3) are the number of grid points constituting the "density shells" $S(\rho_x, a, a')$ and $S(\rho_y, a, a')$, respectively.

Table S1 Values of the Walker-Mezey similarity index $L(\rho_x, \rho_y, 0.1, 10)$ corresponding to the comparisons of the XCSC.0 electron densities obtained with the different basis-sets.

$L(\rho_x, \rho_y, 0.1, 10)$	6-31G	6-311G	6-31G(d)	6-311G(d)
6-31G	100.00			
6-311G	99.49	100.00		
6-31G(d)	96.68	96.65	100.00	
6-311G(d)	96.94	96.99	99.24	100.00

Table S2 Values of the Walker-Mezey similarity index $L(\rho_x, \rho_y, 0.001, 0.1)$ corresponding to the comparisons of the XCSC.0 electron densities obtained with the different basis-sets.

$L(\rho_x, \rho_y, 0.001, 0.1)$	6-31G	6-311G	6-31G(d)	6-311G(d)
6-31G	100.00			
6-311G	96.68	100.00		
6-31G(d)	96.13	94.43	100.00	
6-311G(d)	96.18	96.45	96.76	100.00

Table S3 Values of the Walker-Mezey similarity index $L(\rho_x, \rho_y, 0.1, 10)$ corresponding to the comparisons of all the electron densities obtained with basis-set 6-31G.

$L(\rho_x, \rho_y, 0.1, 10)$	RHF	SC.0	XCSC.0	XC-RHF	SC.1	XCSC.1
RHF	100.00					
SC.0	99.61	100.00				
XCSC.0	99.46	99.53	100.00			
XC-RHF	97.62	97.71	97.87	100.00		
SC.1	97.67	97.86	97.82	99.61	100.00	
XCSC.1	97.52	97.64	97.82	99.80	99.50	100.00

Table S4 Values of the Walker-Mezey similarity index $L(\rho_x, \rho_y, 0.001, 0.1)$ corresponding to the comparisons of all the electron densities obtained with basis-set 6-31G.

$L(\rho_x, \rho_y, 0.001, 0.1)$	RHF	SC.0	XCSC.0	XC-RHF	SC.1	XCSC.1
RHF	100.00					
SC.0	98.54	100.00				
XCSC.0	97.27	97.80	100.00			
XC-RHF	93.40	93.30	93.26	100.00		
SC.1	93.65	94.02	93.02	98.54	100.00	
XCSC.1	92.65	92.72	93.25	98.72	97.54	100.00

Table S5 Values of the Walker-Mezey similarity index $L(\rho_x, \rho_y, 0.1, 10)$ corresponding to the comparisons of all the electron densities obtained with basis-set 6-311G.

$L(\rho_x, \rho_y, 0.1, 10)$	RHF	SC.0	XCSC.0	XC-RHF	SC.1	XCSC.1
RHF	100.00					
SC.0	99.61	100.00				
XCSC.0	99.46	99.53	100.00			
XC-RHF	97.61	97.69	97.82	100.00		
SC.1	97.62	97.82	97.78	99.61	100.00	
XCSC.1	97.54	97.65	97.80	99.84	99.54	100.00

Table S6 Values of the Walker-Mezey similarity index $L(\rho_x, \rho_y, 0.001, 0.1)$ corresponding to the comparisons of all the electron densities obtained with basis-set 6-311G.

$L(\rho_x, \rho_y, 0.001, 0.1)$	RHF	SC.0	XCSC.0	XC-RHF	SC.1	XCSC.1
RHF	100.00					
SC.0	98.38	100.00				
XCSC.0	96.95	97.15	100.00			
XC-RHF	93.37	92.85	93.36	100.00		
SC.1	93.90	94.15	93.05	97.99	100.00	
XCSC.1	92.38	92.07	93.17	98.42	96.81	100.00

Table S7   Values of the Walker-Mezey similarity index $L(\rho_x, \rho_y, 0.1, 10)$ corresponding to the comparisons of all the electron densities obtained with basis-set 6-311G(d).

$L(\rho_x, \rho_y, 0.1, 10)$	RHF	SC.0	XCSC.0	XC-RHF	SC.1	XCSC.1
RHF	100.00					
SC.0	99.61	100.00				
XCSC.0	99.19	99.37	100.00			
XC-RHF	97.20	97.39	97.67	100.00		
SC.1	97.29	97.51	97.67	99.67	100.00	
XCSC.1	97.04	97.24	97.56	99.75	99.52	100.00

Table S8   Values of the Walker-Mezey similarity index $L(\rho_x, \rho_y, 0.001, 0.1)$ corresponding to the comparisons of all the electron densities obtained with basis-set 6-311G(d).

$L(\rho_x, \rho_y, 0.001, 0.1)$	RHF	SC.0	XCSC.0	XC-RHF	SC.1	XCSC.1
RHF	100.00					
SC.0	98.44	100.00				
XCSC.0	96.58	97.46	100.00			
XC-RHF	93.57	93.76	93.35	100.00		
SC.1	94.04	94.36	92.93	98.57	100.00	
XCSC.1	92.32	92.69	93.28	98.12	96.95	100.00

Table S9   Adopted λ-steps for all the X-ray constrained wave function calculations.

	6-31G	6-311G	6-31G(d)	6-311G(d)
XC-RHF	0.01	0.01	0.01	0.01
XCSC.0	0.005	0.005	0.01	0.01
XCSC.1	0.005	0.005	0.01	0.01