

电子的原子散射因子解析表达式的拟合

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提 要

本文用阻尼最小二乘法将国际X射线结晶学手册中全部中性原子的电子散射因子数据,从 $\frac{\sin\theta}{\lambda}$ 等于0.0到2.0的范围内,拟合成包含九个参数的解析式

$$f(s) = \sum_{i=1}^4 a_i e^{-b_i s^2} + c.$$

用相对偏离因子

$$R = \sum_{k=1}^N (f_{ok} + f_{ck}) / \sum_{k=1}^N f_{ok}$$

作为估计原子散射因子计算值与观测值之间相对偏离程度的判据. 计算结果表明, 各种原子散射因子的相对偏离因子 R 约为 10^{-3} . 文中除列出参数表外, 还给出了相对偏离因子、最大误差、平均误差、均方差以及偏差方和.

电子衍射和电子显微分析常用到电子的原子散射因子. 虽然在国际X射线结晶学手册中, 列出了从 $s \left(= \frac{\sin\theta}{\lambda} \right)$ 等于0.0到2.0范围内, 98种中性原子以及一些离子的散射因子值^[1], 但是这些离散的值不便于实际应用. 在用电子计算机来计算电子衍射强度或电子显微象的衬度时, 最好能把原子散射因子写成解析表达式. Smith和Burge^[2]曾用了包含六个参数的解析式来表达电子的原子散射因子. Doyle和Turner^[3]则用了八个参数, 他们求出了一些中性原子和离子的相应参数. 本文用阻尼最小二乘法将国际X射线结晶学手册中全部中性原子的散射因子数据, 拟合成与X射线情形相同的解析表达式^[4], 式中包含九个参数如下:

$$f(s) = \sum_{i=1}^4 a_i e^{-b_i s^2} + c, \quad (1)$$

式中 a_i, b_i, c 为待定参数.

在实际计算中, 把相同元素X射线原子散射因子的九个参数作为待定参数的初值. 为了防止初值参数选得不太合适, 而使迭代过程中出现发散现象, 在残差平方和中引入阻尼因子, 以加快收敛步伐^[5]. 借助相对偏离因子

$$R = \sum_{k=1}^N (f_{ok} - f_{ck}) / \sum_{k=1}^N f_{ok} \quad (2)$$

表1 电子的原子散射因子解析式 $f(s) = \sum_{i=1}^4 a_i e^{-b_i s^2} + c$ 的参数

	a_1	b_1	a_2	b_2	a_3	b_3	a_4	b_4	c	ϵ_{max}	$S_{\epsilon_{max}}$	$\bar{\epsilon}$	σ	R
H	0.04924	1.12357	0.13162	4.81011	0.22993	14.8439	0.11705	39.0726	0.00683	0.005	0.04	0.001	0.001	0.002
He	0.06056	0.69147	0.15040	3.08412	0.15627	9.62423	0.04248	23.5396	0.00819	0.001	1.00	0.000	0.009	0.001
Li	0.18100	1.37982	0.46885	10.0538	1.47726	45.2163	1.13754	128.547	0.02026	0.004	2.00	0.001	0.001	0.001
Be	0.18017	1.11557	0.56677	7.28333	1.44076	26.6073	0.84079	73.1093	0.02330	0.002	2.00	0.001	0.001	0.000
B	0.18848	0.97203	0.64565	5.81321	1.33187	20.0682	0.60166	57.3252	0.02600	0.002	2.00	0.001	0.000	0.000
C	0.23238	1.01435	0.81994	5.78949	1.12081	19.2115	0.39422	54.1132	0.03179	0.002	1.60	0.001	0.001	0.001
N	0.13897	0.52475	0.48164	2.68683	1.06113	9.74277	0.50718	30.7532	0.02179	0.001	0.80	0.001	0.000	0.001
O	0.24115	0.80966	0.66042	3.71987	0.79431	11.1230	0.25232	30.3521	0.03513	0.001	0.65	0.000	0.000	0.000
F	0.23422	0.70369	0.62045	3.09136	0.71679	9.44919	0.19442	26.2880	0.03534	0.001	1.40	0.000	0.000	0.000
Ne	0.23449	0.63245	0.56495	2.64199	0.63292	7.79134	0.18389	21.7321	0.03567	0.001	1.40	0.000	0.000	0.000
Na	0.54110	1.19898	0.90328	6.49087	1.60421	40.7770	1.66459	129.803	0.06161	0.007	2.00	0.003	0.002	0.002
Mg	0.52369	1.08412	0.89281	5.89505	2.10328	29.8227	1.62238	88.1764	0.06365	0.005	2.00	0.002	0.001	0.001
Al	0.56914	1.10085	1.06080	6.73577	2.67657	29.0652	1.50965	90.5010	0.07005	0.007	2.00	0.003	0.001	0.001
Si	0.53363	0.97815	1.08891	5.88225	2.70558	23.3404	1.42748	71.1450	0.06988	0.005	2.00	0.002	0.001	0.001
P	0.50346	0.87932	1.09013	5.13366	2.58035	18.8552	1.24278	54.9233	0.06975	0.004	0.80	0.001	0.001	0.001
S	0.49157	0.82092	1.13064	4.73512	2.42939	16.1274	1.03713	45.3688	0.07118	0.003	2.00	0.001	0.001	0.000
Cl	0.48380	0.77733	1.16254	4.38180	2.26346	14.0357	0.87424	38.5357	0.07318	0.002	0.80	0.001	0.000	0.000
Ar	0.47103	0.72503	1.18116	4.00402	2.09559	12.2894	0.75940	33.0660	0.07339	0.002	0.90	0.001	0.000	0.000
K	0.83435	1.26295	2.57342	8.16010	2.42361	45.7999	3.03079	166.443	0.11302	0.017	2.00	0.007	0.004	0.002
Ca	0.81886	1.19024	2.38629	7.17228	3.38497	39.3149	3.20375	121.103	0.11416	0.014	2.00	0.005	0.003	0.002
Sc	0.82184	1.14499	2.29740	6.56826	3.22554	34.5258	2.84374	108.232	0.11645	0.013	2.00	0.004	0.003	0.001
Ti	0.83718	1.11535	2.22146	6.13917	3.04722	31.4668	2.54718	100.008	0.11901	0.012	2.00	0.004	0.002	0.001
V	0.85465	1.08878	2.14893	5.78576	2.89030	29.2795	2.28594	94.2114	0.12164	0.011	2.00	0.004	0.002	0.001
Cr	0.88038	1.07250	2.09996	5.53692	2.20830	26.8071	1.65155	98.1169	0.12471	0.010	2.00	0.004	0.002	0.001
Mn	0.88646	1.03534	1.99407	5.18729	2.54856	25.4956	1.94847	83.2112	0.12617	0.008	2.00	0.003	0.002	0.001
Fe	0.90628	1.01383	1.92631	4.97780	2.41077	24.2683	1.79055	79.4409	0.12842	0.008	2.00	0.003	0.002	0.001
Co	0.90998	0.97791	1.85730	4.71826	2.28316	22.9255	1.67125	75.6734	0.12965	0.007	2.00	0.003	0.002	0.001
Ni	0.93017	0.96164	1.78977	4.56669	2.16054	21.9676	1.52296	72.4782	0.13262	0.006	2.00	0.003	0.001	0.001
Cu	0.95193	0.94385	1.74900	4.46409	1.64503	21.0681	1.11668	79.6493	0.13474	0.007	2.00	0.003	0.001	0.001
Zn	0.95958	0.91866	1.67373	4.30323	1.95071	20.4870	1.34175	67.4086	0.13659	0.006	2.00	0.002	0.001	0.001
Ga	1.09595	0.99943	1.72261	5.03468	2.61438	24.7417	1.52306	84.9517	0.14866	0.009	2.00	0.004	0.002	0.001
Ge	1.07488	0.95257	1.67658	4.78250	2.87946	22.0912	1.59500	71.1665	0.14870	0.007	2.00	0.003	0.002	0.001
As	1.04029	0.89757	1.61472	4.45901	2.98528	19.0809	1.53121	57.6297	0.14722	0.006	2.00	0.002	0.001	0.001
Se	1.02041	0.85673	1.56993	4.20859	3.02495	16.8080	1.44175	48.6300	0.14656	0.005	2.00	0.002	0.001	0.000
Br	1.00375	0.82180	1.52874	4.01238	2.99457	14.8316	1.38444	41.5922	0.14609	0.004	2.00	0.001	0.001	0.000
Kr	0.98899	0.78947	1.53397	3.88699	2.97758	13.5568	1.24952	37.1324	0.14660	0.004	2.00	0.001	0.001	0.000
Rb	1.42780	1.13570	3.42834	8.55214	2.98652	41.4786	3.72877	173.152	0.19685	0.024	2.00	0.009	0.005	0.002
Sr	1.38199	1.07975	3.32859	7.8631	4.00265	39.6810	4.18667	130.817	0.19625	0.021	2.00	0.008	0.004	0.002
Y	1.34006	1.03163	3.27025	7.15377	4.12802	37.5591	3.72574	112.588	0.19612	0.017	2.00	0.007	0.004	0.002
Zr	1.30145	0.98560	3.22818	6.62142	4.06357	30.6316	3.36196	101.129	0.19601	0.015	2.00	0.006	0.004	0.002
Nb	1.25788	0.93706	3.20895	6.13119	3.55467	26.3035	2.44883	96.6631	0.19452	0.014	0.00	0.006	0.003	0.001
Mo	1.23849	0.90855	3.20473	5.80547	3.44083	24.5162	2.17559	92.2924	0.19570	0.012	2.00	0.005	0.003	0.001
Tc	1.24122	0.90093	3.20720	5.60056	3.64441	24.3207	2.55125	83.6231	0.19366	0.012	0.00	0.005	0.003	0.001
Ru	1.21842	0.87173	3.19676	5.28704	3.12230	21.7096	1.80913	84.2304	0.19377	0.012	0.00	0.004	0.002	0.001
Rh	1.20244	0.85021	3.16863	5.01511	2.96386	20.3657	1.69441	80.6371	0.20136	0.011	0.00	0.004	0.002	0.001

Pd	1.05766	0.72821	2.69010	4.00891	2.64994	13.5298	0.99422	44.4972	0.18384	0.007	0.00	0.002	0.001
As	1.21087	0.83473	3.16064	4.69018	2.66163	19.1689	1.42689	78.9906	0.20701	0.009	2.00	0.004	0.001
Cd	1.22503	0.83438	3.12183	4.55327	2.86597	19.4153	1.89448	69.6184	0.21128	0.009	2.00	0.004	0.001
In	1.35495	0.91033	3.24016	4.91209	3.44836	23.6490	2.15730	85.1136	0.22698	0.013	2.00	0.005	0.001
Sn	1.33656	0.88439	3.11583	4.61908	3.80499	22.0613	2.37062	73.8053	0.22688	0.011	2.00	0.005	0.001
Sb	1.30727	0.85098	2.98093	4.30739	4.04458	20.0491	2.41286	62.3919	0.22472	0.009	2.00	0.004	0.001
Te	1.29090	0.82652	2.85075	4.05350	4.19425	18.1887	2.43357	53.7125	0.22396	0.010	6.00	0.003	0.001
I	1.30488	0.82164	2.76224	3.93610	4.38534	17.1101	2.22441	48.8038	0.22646	0.007	2.00	0.003	0.005
Xe	1.42532	0.87668	2.77836	4.20012	4.53840	17.1970	1.79305	46.9385	0.23859	0.009	2.00	0.002	0.000
Cs	2.21883	1.28716	4.60571	8.64777	4.45838	37.6962	4.92676	189.044	0.29953	0.040	2.00	0.015	0.003
Ba	2.19676	1.25255	4.67806	8.37051	5.20415	39.1838	5.87447	145.486	0.29951	0.037	2.00	0.013	0.002
La	2.13774	1.20939	4.59844	7.83720	5.46274	35.2049	5.28736	126.133	0.29740	0.031	2.00	0.011	0.002
Ce	2.10007	1.17941	4.55426	7.64689	5.28185	34.6029	5.08329	123.673	0.29857	0.030	2.00	0.011	0.006
Pr	2.19312	1.18370	4.52607	7.71494	4.71689	36.6823	5.23029	134.769	0.30398	0.031	2.00	0.012	0.002
Nd	2.18399	1.16032	4.42520	7.46517	4.54596	35.5218	5.12534	131.059	0.30473	0.030	2.00	0.011	0.006
Pm													
Sm	2.18332	1.12260	4.28398	7.13181	4.31155	34.6951	4.78637	128.845	0.30577	0.028	2.00	0.011	0.006
Eu	2.17938	1.10027	4.22665	6.98080	4.23139	34.4883	4.60577	125.712	0.30810	0.028	2.00	0.010	0.006
Gd	2.11999	1.05620	4.09793	6.54065	4.45265	30.8713	4.27187	109.416	0.30556	0.024	2.00	0.009	0.002
Tb	2.19600	1.07789	4.11165	6.79783	4.09941	34.6966	4.22118	124.661	0.31428	0.031	0.00	0.011	0.007
Dy	2.16544	1.04740	3.98593	6.50638	3.90890	32.6372	4.24760	118.443	0.31329	0.024	2.00	0.009	0.005
Ho	2.04431	0.97332	3.74949	5.79447	4.06012	26.7471	4.26511	96.1710	0.30359	0.029	0.04	0.007	0.004
Er	2.15671	1.01427	3.83978	6.24679	3.74202	31.8179	4.06651	114.901	0.31613	0.027	2.00	0.009	0.005
Tm	2.15114	0.99878	3.76811	6.12492	3.65004	31.3490	3.90289	112.622	0.31977	0.024	0.00	0.009	0.005
Yb	2.14582	0.98379	3.70152	6.01377	3.58929	31.0735	3.78259	111.822	0.31964	0.021	2.00	0.008	0.002
Lu	2.07541	0.93824	3.58591	5.61207	3.87601	27.8278	3.61559	96.1033	0.31463	0.018	0.00	0.007	0.004
Hf	2.03115	0.90829	3.51892	5.35170	4.01070	25.4086	3.29314	86.5407	0.31215	0.016	2.00	0.007	0.003
Ta	1.98850	0.87840	3.48239	5.12588	4.07937	23.4938	2.98409	80.1163	0.30946	0.014	2.00	0.006	0.003
W	1.97392	0.86344	3.48896	5.02772	4.08018	22.2866	2.68047	75.7871	0.31075	0.013	2.00	0.006	0.003
Re	1.92672	0.83350	3.44733	4.79095	4.03028	20.4165	2.54236	69.5880	0.30761	0.011	2.00	0.005	0.003
Os	1.90732	0.81707	3.45952	4.68197	3.97995	19.3994	2.32049	66.0742	0.30738	0.012	0.00	0.004	0.001
Ir	1.87864	0.79335	3.46471	4.53871	3.91500	18.3615	2.14741	62.9838	0.30603	0.010	2.00	0.004	0.001
Pt	1.84670	0.77396	3.46733	4.38830	3.61207	16.7894	1.57926	60.4880	0.30430	0.010	0.08	0.004	0.001
Au	1.82271	0.75892	3.47327	4.26626	3.51273	15.9633	1.43598	57.7965	0.30394	0.008	2.00	0.003	0.001
Hs	1.83029	0.75399	3.53807	4.26088	3.60589	16.2594	1.67871	56.3570	0.30863	0.009	2.00	0.003	0.001
Tl	1.93415	0.79990	3.85934	4.66429	3.82418	19.7903	2.05207	74.7244	0.32681	0.012	0.00	0.005	0.001
Pb	1.94124	0.79971	3.85731	4.60863	4.20251	19.8331	2.25982	69.2077	0.33191	0.012	2.00	0.005	0.003
Bi	1.92664	0.78860	3.82543	4.47990	4.52248	19.4982	2.48360	64.7147	0.33331	0.012	2.00	0.005	0.003
Po	1.88230	0.76281	3.71207	4.23226	4.73640	18.1512	2.69494	57.2473	0.32945	0.013	0.00	0.004	0.001
At	1.86076	0.74794	3.63868	4.07523	4.97434	17.3069	2.66395	52.3519	0.32869	0.009	2.00	0.003	0.001
Rn	1.86088	0.74375	3.58711	3.98911	5.18974	16.6754	2.51993	48.6098	0.33168	0.009	2.00	0.003	0.000
Fr	2.60915	1.06688	5.08860	7.01375	5.62536	31.4890	4.93145	171.743	0.42517	0.039	2.00	0.017	0.003
Ra	2.61407	1.05942	5.18681	6.96304	6.02637	32.0739	6.27116	134.285	0.42739	0.038	2.00	0.016	0.002
Ac	2.56421	1.02943	5.10621	6.62342	6.43140	30.0266	5.49285	114.588	0.42435	0.034	2.00	0.014	0.002
Th	2.50061	0.99429	4.98823	6.24105	6.70978	27.5340	5.46739	100.577	0.41959	0.030	2.00	0.012	0.002
Pa	2.55227	1.00772	5.16312	6.35932	6.10216	28.2608	5.29750	107.961	0.42682	0.032	2.00	0.012	0.002
U	2.56086	1.00272	5.20664	6.28157	5.93139	27.9933	4.97860	106.931	0.42920	0.033	2.00	0.012	0.002
NP	2.53867	0.98378	5.15760	6.06470	5.71736	26.8172	4.89271	103.069	0.42879	0.029	2.00	0.012	0.002
Pu	2.57218	0.99197	5.22851	6.06710	5.13516	27.2516	4.79656	112.848	0.43444	0.030	2.00	0.012	0.002
Am	2.57125	0.98329	5.21316	5.94195	4.98168	26.8301	4.61062	110.605	0.43586	0.029	2.00	0.012	0.002
Cm	2.53626	0.96055	5.10320	5.68828	5.21947	25.4359	4.39750	97.5280	0.43314	0.027	2.00	0.010	0.002
Bk	2.54045	0.95368	5.07297	5.57817	5.06255	25.0739	4.27205	95.3855	0.43449	0.025	2.00	0.010	0.002
Cf	2.52859	0.93727	4.94570	5.44570	4.74570	24.4511	5.03828	76.9542	0.43099	0.014	0.00	0.013	0.002

作为估计原子散射因子计算值与观测值之间相对偏离程度的判据。(2)式中 f_{ok} 为国际 X 射线结晶学手册上的原子散射因子值, f_{ck} 为借助(1)式所计算出的值。此外,在计算中还同时求出最大误差

$$\varepsilon_{\max} = \text{Max}_{1 \leq k \leq N} |f_{ok} - f_{ck}| \quad (3)$$

及其相应的 S 值,式中 Max 表示最大值。也求出了平均误差

$$\bar{\varepsilon} = \frac{1}{N} \sum_{k=1}^N |f_{ok} - f_{ck}|, \quad (4)$$

均方差

$$\sigma = \sqrt{\frac{1}{N} \sum_{k=1}^N (\bar{\varepsilon} - |f_{ok} - f_{ck}|)^2} \quad (5)$$

以及偏差方和

$$Q = \sum_{k=1}^N |f_{ok} - f_{ck}|^2. \quad (6)$$

从表 1 可见,各种原子散射因子的相对偏离因子 R 约为 10^{-3} 。这对于一般的计算工作,精度已经足够。

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FITTING THE ATOMIC SCATTERING FACTORS FOR ELECTRONS TO AN ANALYTICAL FORMULA

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ABSTRACT

The data of electron scattering factor for all neutral atoms, given in International Tables for X-Ray Crystallography in the range of $\sin \theta/\lambda$ from 0.0 to 2.0 have been fitted by use of the damping least square method to an analytical formula with nine parameters as

$$f(s) = \sum_{i=1}^4 a_i e^{-b_i s} + c.$$

A relative deviation factor

$$R = \frac{\sum_{k=1}^N |f_{ok} - f_{ck}|}{\sum_{k=1}^N f_{ok}}$$

is served as the criterion of the relative deviation between the calculated and the observed values of the atomic scattering factor. The calculation shows that the relative deviation factors R for all atomic factors are approximately equal to 10^{-3} . All parameters and corresponding relative deviation factors are tabulated. The maximum errors, the mean error, the mean square error and the summation square deviation are also given.