Acta Cryst. (1959). **12**, 7

Calculations of Radially Correlated Atomic Scattering Factors-Extension to Three- and Four-Electron Systems*

By R. P. Hurst[†] and F. A. Matsen

Departments of Chemistry and Physics, The University of Texas, Austin, Texas, U.S.A.

(*Received* 2 *June* 1958 *and in revised form* 5 *August* 1958)

Radially correlated wavefunctions have been used to evaluate the atomic scattering factors for a number of three- and four-electron systems. Radially correlated factors are found to be in good agreement with recent Hartree–Fock results for the lithium and beryllium atoms. It is found that the atomic scattering factor is a sensitive function of the wavefunction parameters. Finally, it is suggested that one can use the type of wavefunction considered here to allow for the effects of non-spherical atoms.

1. Introduction

In an earlier paper, Hurst, Miller & Matsen (1958)[‡], a radially correlated wavefunction is used to evaluate the atomic scattering factors for a number of two-electron ions. In the previous paper as in the present work, correlation is introduced through the use of different orbital exponents for atomic orbitals differing otherwise only by the accompanying spin functions. That is, for example, the unnormalized function used to obtain scattering factors for the helium-like ions (see Hylleraas (1929), Eckart (1930))

$$\Psi_o(1,2) = {}^{\S}\begin{pmatrix} ab \\ \alpha\beta \end{pmatrix} + \begin{pmatrix} ba \\ \alpha\beta \end{pmatrix},\quad a = \left(\frac{\mathbf{a}^3}{\pi}\right)^{\frac{1}{2}} \exp\,[-\mathbf{a}r_i],$$

$$b = \left(\frac{\mathbf{b}^3}{\pi}\right)^{\frac{1}{2}} \exp\,[-\mathbf{b}r_i] \quad (1a,\ 1b,\ 1c) \qquad (1)$$

includes some radial correlation while the less general form of this function

$$\Psi_c(1,2) = 2\begin{pmatrix} cc \\ \alpha\beta \end{pmatrix},\quad c = \left(\frac{\mathbf{c}^3}{\pi}\right)^{\frac{1}{2}} \exp\,[-\mathbf{c}r_i] \quad (2a,\ 2b) \qquad (2)$$

obtained by requiring the condition on the orbital exponents $\mathbf{a} = \mathbf{b} = \mathbf{c}$ is uncorrelated. In keeping with terminology adopted by previous authors, the wavefunctions of the type illustrated by $\Psi_o(1,2)$ shall be called 'Open-Configuration Wavefunctions' and functions of the type illustrated by $\Psi_c(1,2)$ 'Closed-Configuration Wavefunctions'.

Recent open-configuration energy calculations have given, with few exceptions, lower energies than were obtained in the presently available Hartree–Fock results. For example, Shull & Löwdin (1956) have found this true for a number of helium-like ions; Brigman & Matsen (1957) found this for lithium; and Brigman, Hurst, Gray & Matsen (1958) found this for the beryllium atom. Since the energies are frequently better, one can reasonably suppose that the open-configuration scattering factors may be more reliable than the difficult to compute Hartree–Fock factors.

The present effort is to consider the feasibility of using open-configuration wavefunctions to obtain atomic scattering factors for many-electron systems. To this end, open-configuration calculations for a number of three- and four-electron systems are presented and are compared with the corresponding closed-configuration factors and with recent Hartree–Fock factors obtained by previous writers.

2. Methods and calculations

In this work the scattering factors are computed from (see James (1948))

$$f = \frac{\int \Psi^* \left(\sum_k \exp\,[i\mu \cos \alpha_k r_k]\right) \Psi d\tau}{\int \Psi^* \Psi d\tau}, \qquad (3a)$$

where

$$\mu = 4\pi \sin \theta/\lambda \qquad (3b)$$

and

$$d\tau = d\tau_1 d\tau_2 \ldots d\tau_n \qquad (3c)$$

and

$$d\tau_k = r_k^2 \sin \alpha_k d\alpha_k d\theta_k dr_k\,. \qquad (3d)$$

The unnormalized wavefunction Ψ used in the three-electron ion calculations is the doublet-state open-configuration function given by

$$\Psi = \begin{pmatrix} cab \\ \alpha\alpha\beta \end{pmatrix} + \begin{pmatrix} cba \\ \alpha\alpha\beta \end{pmatrix} \qquad (4)$$

---

* This research was supported by the Robert A. Welch Foundation of Houston, Texas, and the Office of Ordnance Research, U.S. Army.

[†] Present address: The University of Wisconsin, Naval Research Laboratory, Madison, Wisconsin.

[‡] Formula (6*a*) of this paper should read:

$$f = \left\{\frac{32\mathbf{a}^4}{(4\mathbf{a}+\mu)^2} + \frac{256(\mathbf{ab})^3}{\{(\mathbf{a}+\mathbf{b})^2+\mu^2\}^2(\mathbf{a}+\mathbf{b})^2} + \frac{32\mathbf{b}^4}{(4\mathbf{b}^2+\mu^2)^2}\right\}\frac{1}{N}$$

[§] $\begin{pmatrix} ab \\ \alpha\beta \end{pmatrix} = \frac{1}{\sqrt{2!}}\begin{vmatrix} (a\alpha)_1(b\beta)_1 \\ (a\alpha)_2(b\beta)_2 \end{vmatrix}\,.$

and in the case of the four-electron calculations Ψ is the singlet-state function given by

$$\Psi = \begin{pmatrix} acdb \\ \alpha\alpha\beta\beta \end{pmatrix} + \begin{pmatrix} adcb \\ \alpha\alpha\beta\beta \end{pmatrix} + \begin{pmatrix} cbad \\ \alpha\alpha\beta\beta \end{pmatrix} + \begin{pmatrix} bdca \\ \alpha\alpha\beta\beta \end{pmatrix}. \quad (5)$$

In both of these wavefunctions, the letters a, b, c, and d refer to the following Slater orbitals:

$$a = \Psi_{1s}(\mathbf{a}) = \left(\frac{\mathbf{a}^3}{\pi}\right)^{\frac{1}{2}} \exp\left[-\mathbf{a}r\right], \quad (6a)$$

$$b = \Psi_{1s}(\mathbf{b}) = \left(\frac{\mathbf{b}^3}{\pi}\right)^{\frac{1}{2}} \exp\left[-\mathbf{b}r\right], \quad (6b)$$

$$c = \Psi_{2s}(\mathbf{c}) = \left(\frac{\mathbf{c}^5}{3\pi}\right)^{\frac{1}{2}} r \exp\left[-\mathbf{c}r\right], \quad (6c)$$

$$d = \Psi_{2s}(\mathbf{d}) = \left(\frac{\mathbf{d}^5}{3\pi}\right)^{\frac{1}{2}} r \exp\left[-\mathbf{d}r\right]. \quad (6d)$$

The corresponding closed-configuration functions may be obtained from equations (4) and (5) by placing the proper restrictions on the orbital exponents $\mathbf{a}, \mathbf{b}, \mathbf{c}$, and $\mathbf{d}$. That is, in the case of the lithium-like ion calculations, if one requires the condition $\mathbf{a} = \mathbf{b}$ one obtains

$$\Psi = \begin{pmatrix} aac \\ \alpha\beta\alpha \end{pmatrix} + \begin{pmatrix} aac \\ \alpha\beta\alpha \end{pmatrix} = 2\begin{pmatrix} aac \\ \alpha\beta\alpha \end{pmatrix}$$

$$= \frac{2}{\sqrt{3!}} \begin{vmatrix} (a\alpha)_1, & (a\beta)_1, & (c\alpha)_1 \\ (a\alpha)_2, & (a\beta)_2, & (c\alpha)_2 \\ (a\alpha)_3, & (a\beta)_3, & (c\alpha)_3 \end{vmatrix}, \quad (7)$$

which is twice the usual antisymmetric Slater product function making up the closed-configuration wavefunction. Again, for beryllium-like ions the requirement $\mathbf{a} = \mathbf{b}$ and $\mathbf{c} = \mathbf{d}$ reduces the wavefunction to the single determinant

$$\Psi = 4\begin{pmatrix} aadd \\ \alpha\beta\alpha\beta \end{pmatrix}. \quad (8)$$

Spin orthogonality reductions were made in the usual way (see Eyring, Walter, Kimball (1944)) and

Table 1. *Integral formulae for open-configuration atomic scattering factor calculations*

$$^{*}\, S(a, b) = \frac{8(\mathbf{ab})^{3/2}}{(\mathbf{a}+\mathbf{b})^3}$$

$$S(a, c) = \frac{8(3\mathbf{a}^3\mathbf{c}^5)^{1/2}}{(\mathbf{a}+\mathbf{c})^4}$$

$$S(c, d) = \frac{32(\mathbf{cd})^{5/2}}{(\mathbf{c}+\mathbf{d})^5}$$

$$^{\dagger}\, (a/R/b) = \frac{8(\mathbf{ab})^{3/2}(\mathbf{a}+\mathbf{b})}{[(\mathbf{a}+\mathbf{b})^2+\mu^2]^2}$$

$$(a/R/c) = 8\left(\frac{\mathbf{a}^3\mathbf{c}^5}{3}\right)^{1/2} \frac{3[(\mathbf{a}+\mathbf{c})^2-\mu^2]}{[(\mathbf{a}+\mathbf{c})^2+\mu^2]^3}$$

$$(c/R/d) = \frac{32(\mathbf{cd})^{5/2}[(\mathbf{c}+\mathbf{d})^2-\mu^2](\mathbf{c}+\mathbf{d})}{[(\mathbf{c}+\mathbf{d})^2+\mu^2]^4}$$

* $\mathrm{S}(a, b) = \int ab\,d\tau_j = \int \Psi_{1s}(\mathbf{a})\Psi_{1s}(\mathbf{b})\,d\tau_j.$

† $(a/R/b) = \int a[\exp i\mu \cos \alpha r_j]b\,d\tau_j$

$= \int \Psi_{1s}(\mathbf{a}) \exp\left[i\mu \cos \alpha r_j\right] \Psi_{1s}(\mathbf{b})\,d\tau_j$ (atomic units).

Table 2. *Open-configuration atomic scattering factors for lithium-like ions*

$(\sin\theta/\lambda)$ Å^{-1}	He^-	Li	Be^+	B^{++}	C^{+++}	N^{++++}
0·00	3·000	3·000	3·000	3·000	3·000	3·000
0·05	1·955	2·693	2·877	2·933	2·958	2·971
0·10	1·832	2·198	2·583	2·757	2·842	2·890
0·15	1·654	1·901	2·267	2·524	2·676	2·768
0·20	1·452	1·746	2·017	2·290	2·487	2·619
0·25	1·249	1·629	1·843	2·088	2·300	2·461
0·30	1·058	1·513	1·721	1·928	2·133	2·306
0·35	0·8889	1·392	1·624	1·804	1·991	2·164
0·40	0·7424	1·269	1·535	1·707	1·874	2·038
0·45	0·6184	1·148	1·449	1·625	1·777	1·929
0·50	0·5147	1·033	1·362	1·552	1·697	1·837
0·55	0·4287	0·9250	1·275	1·482	1·627	1·758
0·60	0·3577	0·8257	1·188	1·414	1·564	1·690
0·65	0·2992	0·7354	1·104	1·346	1·505	1·629
0·70	0·2511	0·6539	1·022	1·278	1·447	1·573
0·75	0·2114	0·5810	0·9436	1·211	1·391	1·521
0·80	0·1787	0·5160	0·8695	1·144	1·335	1·472
0·85	0·1517	0·4583	0·7998	1·079	1·280	1·423
0·90	0·1292	0·4073	0·7347	1·016	1·225	1·375
0·95	0·1106	0·3622	0·6743	0·9544	1·170	1·328
1·00	0·09499	0·3225	0·6184	0·8955	1·116	1·281
1·05	0·08192	0·2875	0·5669	0·8392	1·063	1·234
1·10	0·07092	0·2566	0·5195	0·7856	1·012	1·188
1·15	0·06163	0·2293	0·4761	0·7348	0·9614	1·142
1·20	0·05376	0·2053	0·4364	0·6868	0·9126	1·097
1·25	0·04706	0·1841	0·4002	0·6416	0·8655	1·052
1·30	0·04134	0·1654	0·3670	0·5991	0·8201	1·009

Table 3. *Open-configuration atomic scattering factors for beryllium-like ions*

$(\sin\theta/\lambda)$ Å^{-1}	Li^-	Be	B^+	C^{++}	N^{+++}
0·00	4·000	4·000	4·000	4·000	4·000
0·05	2·881	3·695	3·852	3·911	3·941
0·10	2·176	3·038	3·471	3·667	3·772
0·15	1·888	2·437	2·994	3·325	3·523
0·20	1·743	2·048	2·551	2·953	3·227
0·25	1·629	1·829	2·205	2·604	2·922
0·30	1·514	1·701	1·962	2·310	2·635
0·35	1·392	1·609	1·799	2·080	2·382
0·40	1·269	1·528	1·688	1·907	2·172
0·45	1·149	1·447	1·605	1·780	2·003
0·50	1·033	1·364	1·536	1·685	1·869
0·55	0·9254	1·280	1·473	1·610	1·765
0·60	0·8260	1·195	1·410	1·548	1·682
0·65	0·7356	1·111	1·347	1·492	1·615
0·70	0·6541	1·030	1·283	1·440	1·558
0·75	0·5812	0·9514	1·219	1·388	1·508
0·80	0·5162	0·8770	1·154	1·337	1·461
0·85	0·4585	0·8071	1·091	1·286	1·417
0·90	0·4075	0·7416	1·028	1·234	1·373
0·95	0·3624	0·6808	0·9671	1·182	1·330
1·00	0·3227	0·6244	0·9083	1·130	1·287
1·05	0·2876	0·5725	0·8518	1·078	1·243
1·10	0·2567	0·5248	0·7980	1·028	1·199
1·15	0·2295	0·4810	0·7468	0·9779	1·156
1·20	0·2054	0·4409	0·6983	0·9294	1·112
1·25	0·1842	0·4043	0·6527	0·8824	1·069
1·30	0·1655	0·3708	0·6097	0·8369	1·027

the scattering integrals (equations (3)) were evaluated in a straightforward manner as is described elsewhere (see Hurst (1958)). Formulae for the required one-electron integrals over the Slater atomic functions are given in Table 1.

During the course of this work, it was found that the atomic scattering factor curve is a sensitive function of the orbital exponents, especially for small values of $\sin\theta/\lambda$. Numerically it was found that for some arguments scattering factors are no more accurate than the choice of orbital exponents. The manner by which these exponents were obtained to the required accuracy, and the numerical values used in the factor calculations have been reported previously (see Hurst, Gray, Brigman & Matsen (1958), and Brigman, Hurst, Gray & Matsen (1958)).

Finally, all numerical work was performed on an IBM CPC computer.

3. Results

In Tables 2 and 3 are given the open-configuration factors for the three- and four-electron ions, respectively. The open-configuration results for the lithium-like ions are compared with the corresponding closed-

Table 4. *Comparison of atomic scattering factors for lithium-like ions*

$(\sin\theta/\lambda)$ Å^{-1}	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9	1·0	1·1	1·2	1·3	
He$^-$	3·00	1·83	1·45	1·06	0·74	0·51	0·36	0·25	0·18	0·13	0·095	0·071	0·054	0·041	*O*
	3·00	1·85	1·50	1·10	0·76	0·52	0·35	0·24	0·16	0·12	0·084	0·062	0·046	0·035	*C*
Li	3·00	2·22	1·74	1·51	1·27	1·03	0·82	0·65	0·51	0·40	0·32	0·26	0·21	0·16	*H–F*
	3·00	2·20	1·75	1·51	1·27	1·03	0·83	0·65	0·52	0·41	0·32	0·26	0·21	0·17	O
	3·00	2·20	1·76	1·54	1·29	1·05	0·84	0·66	0·52	0·40	0·32	0·25	0·20	0·16	*C*
Be$^+$	3·00	2·58	2·02	1·72	1·54	1·36	1·19	1·02	0·87	0·73	0·62	0·52	0·44	0·37	*O*
	3·00	2·59	2·03	1·73	1·55	1·38	1·20	1·04	0·88	0·74	0·62	0·52	0·43	0·36	*C*
B^{++}	3·00	2·76	2·29	1·93	1·71	1·55	1·41	1·28	1·14	1·02	0·90	0·79	0·69	0·60	*O*
	3·00	2·76	2·29	1·94	1·72	1·56	1·43	1·29	1·16	1·03	0·90	0·79	0·69	0·60	*C*
C^{+++}	3·00	2·84	2·49	2·13	1·87	1·70	1·56	1·45	1·34	1·22	1·12	1·01	0·91	0·82	*O*
	3·00	2·84	2·49	2·14	1·88	1·70	1·57	1·46	1·34	1·23	1·13	1·02	0·92	0·83	*C*
N^{++++}	3·00	2·89	2·62	2·31	2·04	1·84	1·69	1·57	1·47	1·38	1·28	1·19	1·10	1·01	*O*
	3·00	2·89	2·62	2·31	2·04	1·84	1·70	1·58	1·48	1·38	1·29	1·20	1·10	1·02	*C*

O = Open-configuration. *C* = Closed-configuration. *H–F* = Hartree–Fock Berghuis *et al.* (1955).

Table 5. *Comparison of atomic scattering factors for beryllium-like ions*

$(\sin\theta/\lambda)$ Å^{-1}	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9	1·0	1·1	1·2	1·3	
Li$^-$	4·00	2·18	1·74	1·51	1·27	1·03	0·83	0·65	0·52	0·41	0·32	0·26	0·21	0·17	*O*
	4·00	2·16	1·74	1·54	1·30	1·05	0·84	0·66	0·52	0·40	0·32	0·25	0·20	0·16	*C*
Be	4·00	3·07	2·06	1·69	1·52	1·36	1·20	1·03	0·88	0·74	0·62	0·52	0·44	0·37	*H–F*
	4·00	3·04	2·05	1·70	1·53	1·36	1·19	1·03	0·88	0·74	0·62	0·52	0·44	0·37	*O*
	4·00	3·06	2·05	1·71	1·54	1·38	1·21	1·04	0·89	0·75	0·63	0·53	0·44	0·37	*C*
B$^+$	4·00	3·47	2·55	1·96	1·69	1·54	1·41	1·28	1·15	1·03	0·91	0·80	0·70	0·61	*O*
	4·00	3·47	2·56	1·97	1·70	1·55	1·42	1·29	1·17	1·04	0·92	0·80	0·70	0·61	*C*
C^{++}	4·00	3·67	2·95	2·31	1·91	1·68	1·55	1·44	1·34	1·23	1·13	1·03	0·93	0·84	*O*
	4·00	3·67	2·96	2·32	1·91	1·69	1·56	1·45	1·35	1·24	1·14	1·03	0·94	0·84	*C*
N^{+++}	4·00	3·77	3·23	2·63	2·17	1·87	1·68	1·56	1·46	1·37	1·29	1·20	1·11	1·03	*O*
	4·00	3·77	3·23	2·64	2·18	1·88	1·69	1·56	1·47	1·38	1·29	1·21	1·12	1·03	*C*

O = Open-configuration. *C* = Closed-configuration. *H–F* = Hartree–Fock Berghuis *et al.* (1955).

Table 6. *Computed energies and optimum orbital exponents for lithium-like ions*

	Open configuration				Closed configuration		
	a	b	c	Energy (a.u.)*	a	c	Energy (a.u.)*
He$^-$	2·1832	1·1886	$9{\cdot}3750\times10^{-7}$	− 2·8757	1·6875	0·0002749	− 2·8477
Li	3·2982	2·0678	0·63896	− 7·4436	2·6864	0·63733	− 7·4179
Be$^+$	4·3921	2·9623	1·0875	−14·2826	3·6819	1·0860	−14·2584
B^{2+}	5·4602	3·8815	1·5214	−23·3726	4·6759	1·5208	−23·3498
C^{3+}	6·5289	4·8018	1·9503	−34·7112	5·6701	1·9505	−34·6899
N^{4+}	7·5816	5·7353	2·3771	−48·2977	6·6636	2·3776	−48·2776

* Units μ_Z/μ_H (27·190) e.v.

Table 7. *Computed energies and optimum orbital exponents for beryllium-like ions*

	Open configuration					Closed configuration		
	a	**b**	**c**	**d**	Energy (a.u.)*	**a**	**d**	Energy (a.u.)*
Li^-	3·2992	2·0677	0·65922	0·24964	− 7·4469	2·6888	0·48530	− 7·4108
Be	4·3956	2·9570	1·1044	0·80788	−14·5815	3·6848	0·95601	−14·5567
B^+	5·4788	3·8522	1·4474	1·3534	−24·2353	4·6764	1·3968	−24·2136
C^{++}	6·5248	4·7840	1·8481	1·8176	−36·3903	5·6651	1·8298	−36·3688
N^{+++}	7·5806	5·7007	2·2825	2·2396	−51·0420	6·6537	2·2592	−51·0240

* Units μ_Z/μ_H (27·190) e.v.

configuration and SCF factors in Table 4. The same type of comparison made in Table 4 for the lithium-like ions is given for beryllium-like ions in Table 5. Finally, the optimum orbital exponents and computed energies upon which the results and conclusions of this work are based are given in Tables 6 and 7 for the three- and four-electron ions, respectively.

4. Discussion

The open-configuration method appears to show promise as a way to improve atomic scattering factors. This assertion is based entirely on the comparison with the widely accepted Hartree–Fock SCF method. See, for example, James (1948).

Perhaps the most important fact noted from this study is that the open-configuration factors for lithium and beryllium agree with the corresponding Hartree–Fock factors almost within the limit of the computational error in the Hartree–Fock factors. According to Berghuis *et al.* (1955) who performed the numerical integrations to obtain the SCF factors 'the last place, of course, does not have any physical significance but facilitates interpolation ...'. That this must be true is easily seen from the fact that the Hartree–Fock fields from which the factor calculations were made are given to but four significant figures, while in the Berghuis paper, the factors themselves are expressed to four figures. This was the justification for rounding the factors in Tables 3 and 4 to the nearest hundredth. In addition, it is possible that the disparity which is noted which exceeds numerical error may represent some small improvement over the SCF factors.

The fact that there is good agreement between these factors and the Hartree–Fock factors is indeed encouraging. First of all, the open-configuration wavefunctions are generally less difficult to obtain than the Hartree–Fock fields. Secondly, evaluation of the scattering integrals is generally somewhat less laborious than in the case of SCF calculations. For example, if one wishes to compute scattering factors from a numerical Hartree–Fock field, numerous troublesome numerical integrations are required. In addition, obtaining scattering factors from analytical Hartree–Fock functions is frequently more laborious than using the simpler antisymmetric atomic orbital product functions.

Finally, quite apart from the possible improvement resulting from including radial-electron correlation and the possible reduction in labor obtained by using orbitals, the open-configuration method does allow one to consider non-spherically symmetric atoms as is often the case for more than four electrons. This, of course, is not possible with presently available spherically symmetric Hartree–Fock functions but is not unique for open-configuration wavefunctions. McWeeny (1951) has previously done this for closed-configuration functions for the first row atoms of the periodic table. Such calculations have recently been extended as far as Ca^{2+} by Tomiie & Stam (1958).

Note added in proof. — Dr J. N. Silverman has kindly called to the authors attention results of Ibers' work which were inadvertently overlooked at the writing of this paper. In particular, Ibers (1957) has published Hartree-Fock factors using two- and three-configuration distributions for Be and B atoms, respectively. The function Ibers used for Be gave a better energy than that computed from the open configuration function of the present work, namely it gave −14.642 a. u. Further, Ibers' factors showed a maximum deviation of about 0.03 electrons from the present radially correlated results for Be.

References

Berghuis, J., Haanappel, IJ. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. & Veenendaal, A. L. (1955). *Acta Cryst.* **8**, 478.

Brigman, G. H., Hurst, R. P., Gray. J. D. & Matsen, F. A. (1958). *J. Chem. Phys.* **29**, 251.

Brigman, G. H. & Matsen, F. A. (1957). *J. Chem. Phys.* **27**, 829.

Eckart, C. (1930). *Phys. Rev.* **36**, 878.

Eyring, H., Walter, J. & Kimball, G. E. (1944). *Quantum Chemistry*, p. 240. New York: Wiley.

Hurst, R. P. (1958). *Calculations of Coherent Atomic Scattering Factors From Open Configuration Wave Functions.* Ph.D. Dissertation, The University of Texas,

Hurst, R. P., Gray, J. D., Brigman, G. H. & Matsen, F. A.(1958) . *Mol. Phys.* **1**, 189.

Hurst, R. P., Miller, J. & Matsen, F. A. (1958). *Acta Cryst.* **11**, 320.

Hylleraas, E. A. (1929). *Z. Physik*, **54**, 347.

Ibers, J. A. (1957). *Acta cryst.* **10**, 86.

James, R. W. (1948). *The Optical Principles of The Diffraction of X-Rays*, p. 129. London: Bell.

James, R. W. & Brindley, G. W. (1931). *Phil. Mag.* **12**, 104.

McWeeny, R. (1951). *Acta Cryst.* **4**, 513.

Shull, H. & Löwdin, P. O. (1956). *J. Chem. Phys.* **25**, 1035.

Tomiie, Y. & Stam, C. H. (1958). *Acta Cryst.* **11**, 126.