examination of correlation effects in negative ions of crystallographic interest would be most valuable.

Great thanks are due to Dr S. F. Boys for his kindness in providing the numerical coefficients D of equation (3), and also to Dr A. C. Hurley for advice and many helpful discussions on poly-detor calculations.

References

Allen, L. C. (1957). Quarterly Progress Report, Solid State and Molecular Theory Group, M.I.T., July 15, p. 52. (Unpublished.)

Batterman, B. W. (1959*a*). *Phys. Rev. Letters*, **2**, 47.

Batterman, B. W. (1959*b*). *Phys. Rev.* **115**, 81.

Bernal, M. J. M. & Boys, S. F. (1952*a*). *Philos. Trans.* A, **245**, 116.

Bernal, M. J. M. & Boys, S. F. (1952*b*). *Philos. Trans.* A, **245**, 139.

Boys, S. F. & Price, V. E. (1954). *Philos. Trans.* A, **246**, 451.

Dawson, B. (1960). *Acta Cryst.* **13**, 403.

Dawson, B. (1961). *Acta Cryst.* **14**. 1120.

Freeman, A. J. (1959). *Acta Cryst.* **12**, 261.

Freeman, A. J. (1960). *Acta Cryst.* **13**, 190.

Froese, C. (1957). *Proc. Camb. Phil. Soc.* **53**, 206.

Fröman, A. (1958). *Phys. Rev.* **112**, 870.

Glembotskii, I. I., Kibartas, V. V. & Iutsis, A. P. (1955). *J. Exp. Theor. Phys.* **29**, 617. (*Soviet Physics JETP*. (1956). **2**, 476.)

Green, L. C., Stephens, C., Kolchin, E. K., Chen, C. C., Rush, P. P. & Ufford, C. W. (1959). *J. Chem. Phys.* **30**, 1061.

Hartree, D. R. & Hartree, W. (1938). *Proc. Roy. Soc.* A, **166**, 450.

Hartree, D. R. & Hartree, W. (1948). *Proc. Roy. Soc.* A, **193**, 299.

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

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

Kibartas, V. V., Kavetskis, V. I. & Iutsis, A. P. (1955). *J. Exp. Theor. Phys.* **29**, 623. (*Soviet Physics JETP*. (1956). **2**, 481.)

Kittel, C. (1956). *Introduction to Solid State Physics*, p. 209. New York: Wiley.

Komura, Y., Tomiie, Y. & Nathans, R. (1959). *Phys. Rev.* (*Letters*), **3**, 268.

Löwdin, P.-O. & Rèdei, L. (1959). *Phys. Rev.* **114**, 752.

McDonald, T. R. R. (1960). *Acta Cryst.* **13**, 113.

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

Weiss, R. J. & deMarco, J. J. (1958). *Rev. Mod. Phys.* **30**, 59.

Worsley, B. H. (1958). *Canad. J. Phys.* **36**, 289.

Worsley, B. H. (1959). *Canad. J. Phys.* **37**, 967.

Acta Cryst. (1961). **14**, 1120

Atomic Scattering Amplitudes for Electrons for Some of the Lighter Elements

By B. Dawson

Division of Chemical Physics, C.S.I.R.O. Chemical Research Laboratories, Melbourne, Australia

(*Received* 9 *August* 1960 *and in revised form* 21 *February* 1961)

Theoretical mean square radii $\langle r^2\rangle$ for the atomic charge distributions given by poly-detor, Hartree–Fock and Slater function calculations are used in conjunction with evidence of experimental $\langle r^2\rangle$ values given by diamagnetic susceptibility measurements to obtain improved estimates of the atomic scattering amplitudes, at zero scattering angle, which apply to the elements F–Ca, and also Kr, in the first Born approximation. Values of the scattering amplitudes at other scattering angles are also obtained, and the new results are compared with results obtained earlier by Ibers (1958) and Vainshtein & Ibers (1958).

In terms of the first Born approximation to the scattering of electrons by neutral spherically symmetric atoms, the atomic scattering amplitudes for electrons $f_{\text{el.}}(s)$ are real and related to the atomic scattering factors for X-rays $f(s)$ by

$$f_{\text{el.}}(s)=(8\pi^2me^2/h^2)(Z-f(s))/s^2, \quad (1)$$

where

$$f(s)=\int_0^\infty 4\pi r^2\varrho(r)\,\sin sr/sr\,dr \quad (2)$$

and $4\pi r^2\varrho(r)$ is the radial charge density, $s=4\pi\sin\theta/\lambda$ and Z is the atomic number. (For discussion of equation (1) in terms of the true complex scattering amplitude, see e.g. Cowley & Rees (1958)). Ibers (1958) has recently considered the suitability of the real $f_{\text{el.}}(s)$ when applied to the interpretation of electron-diffraction data obtained from solids, concluding that the use of the first Born approximation is at present adequate for such purposes, provided that reliable values of $f(s)$ are available for the derivation of $f_{\text{el.}}(s)$ in the region where s is small. For $f_{\text{el.}}(0)$, he has shown that the uncertainties which are associated with equation (1) because of the need to extrapolate from $f_{\text{el.}}(s)$ values for s small can be avoided since

$$f_{\text{el.}}(0)=(4\pi^2me^2/3h^2)\langle r^2\rangle\ , \quad (3)$$

where $\langle r^2\rangle$, the mean square radius of the atomic charge distribution, is

Table 1. $\langle r^2 \rangle$ *values* (*a.u.*)

(*A*)—Theoretical and experimental

		F	Ne	Na	Mg	Al	Si	P	S	Cl	A	K	Ca	Kr
$\langle r^2 \rangle_{\text{neon core}}$	HF	—	9·41^{a}	6·42^{b}, Na^{+}	4·73^{c}, Mg^{+2}	3·64^{d}, Al^{+3}	—	—	—	1·71^{e}, Cl^{-}	1·47^{f}	1·28^{f}, K^{+}	—	0·280^{g}
	S	—	7·158	5·237	3·999	3·154	2·552	2·107	1·769	1·507	1·299	—	—	—
$\langle r^2 \rangle_{3s}$	HF	—	—	20·76^{b} 19·53^{h}	11·91^{i}	6·82^{d}, Al^{+1}	3·98^{j}, Si^{+3}	—	—	3·01^{e}, Cl^{-}	2·35^{f}	1·881^{f}, K^{+}	—	0·332^{g}
	S	—	—	26·186	15·665	10·436	7·455	5·595	4·356	3·488	2·857	—	—	—
$\langle r^2 \rangle_{3p}$	HF	—	—	—	—	14·00^{h}	7·21^{h}, Si^{+1}	—	—	—	3·31^{f}	2·41^{f}, K^{+}	—	0·343^{g}
	S	—	—	—	—	10·436	7·455	5·595	4·356	3·488	2·857	—	—	—
$\langle r^2 \rangle_{4s}$	HF	—	—	—	—	—	—	—	—	—	—	32·13^{k} 27·80^{h}	20·605^{l}	2·492^{g}
$\langle r^2 \rangle_{4p}$	HF	—	—	—	—	—	—	—	—	—	—	—	—	4·452^{g}
$\langle r^2 \rangle_{3d}$	HF	—	—	—	—	—	—	—	—	—	—	—	—	0·455^{g}
$\langle r^2 \rangle_{\text{total}}$, neutral atom	HF	10·24^{m}	9·41^{a}	27·17^{b} 25·94$^{b, h}$	28·56$^{c, i}$	—	—	—	—	—	26·03^{f}	51·65$^{f, k}$ 47·32$^{f, h}$	56·63^{l}	39·25^{g}
	S	—	7·16	31·42	35·33	34·46	32·37	30·08	27·91	25·92	24·16	—	—	—
	PD	—	9·150	—	—	—	—	—	25·65	25·32	—	—	—	—
	PDRF	—	9·207	—	—	—	—	—	25·08	25·77	—	—	—	—
	Exp	—	9·1	—	—	—	—	—	—	—	24·5	—	—	35·5

(*B*)—Estimated (from Fig. 1)

		Mg	Al	Si	P	S	Cl	A
$\langle r^2 \rangle_{\text{neon core}}$,	curve *A*	4·74	3·64	2·9	2·4	2·0	1·7	1·47
$\langle r^2 \rangle_{3s}$,	curve *B*	11·91	7·1	4·9	3·7$_{5}$	3·0	2·6	2·25
$\langle r^2 \rangle_{3p}$,	curve *C*	—	15·5	9·3	6·3	4·7	3·7	3·1
$\langle r^2 \rangle_{\text{total}}$,	curve *D*	28·56	33·34	31·3	28·8	26·8	25·4	24·57

[a] Worsley (1958*a*)
[b] Hartree & Hartree (1948)
[c] Jost (1940)
[d] Froese (1957)
[e] Hartree & Hartree (1936)
[f] Hartree & Hartree (1938*a*)
[g] Worsley (1958*b*)
[h] Biermann & Lübeck (1948)
[i] Biermann & Trefftz (1949)
[j] Hartree, Hartree & Manning (1941)
[k] Hartree & Hartree (1938*b*)
[l] Hartree & Hartree (1938*c*)
[m] Allen (1957)

$$\langle r^2 \rangle = \int_0^\infty r^2 [4\pi r^2 \varrho(r)] dr \,. \qquad (4)$$

Using results obtained with equations (2) and (4) from self-consistent field (SCF) calculations with and without exchange (the Hartree–Fock and Hartree approximations, respectively), he has derived new values of $f_{\text{el.}}(s)$ for many of the lighter atoms. For heavier atoms, new values of $f_{\text{el.}}(s)$ were derived from the Thomas–Fermi–Dirac statistical model. Because of the absence of SCF data for the elements Al to Cl inclusive, values of $f_{\text{el.}}(s)$ for these atoms were omitted by Ibers (1958). To fill this gap, Vainshtein & Ibers (1958) have reported values based largely on Tomiie & Stam's (1958) f-curves derived from Slater functions. For the $f_{\text{el.}}(0)$ values appropriate to the Slater functions, extrapolation from $f_{\text{el.}}(s)$ results for s small was employed.

The present work attempts to provide more reliable estimates of $f_{\text{el.}}(0)$, and also $f_{\text{el.}}(s)$, for the neutral atoms of the third chemical period by using: (*a*), $\langle r^2 \rangle$ values obtained from Hartree–Fock data that are available for ionized states of some of these atoms; (*b*), $\langle r^2 \rangle$ values obtained from poly-detor calculations for the neutral states of some of these atoms; (*c*), $\langle r^2 \rangle$ values obtained from the Slater functions of these neutral atoms by calculation rather than by the extrapolation noted above; (*d*), the values $\langle r^2 \rangle_{\text{exp.}}$ suggested by measurements of molar diamagnetic susceptibility. In addition, new values of $f_{\text{el.}}(s)$ are obtained for neutral F, Ne, K and Kr.

The values of $\langle r^2 \rangle$ used in the present work are given in Table 1, together with (in most instances) the source of these values. In the case of the Hartree–Fock values, these were obtained by numerical integration of equation (4) using r-intervals sufficiently fine to ensure adequacy of the integration procedure: where values of $4\pi r^2 \varrho(r)$ additional to those given in the original sources were required, these were obtained by Lagrangian interpolation. The Slater function $\langle r^2 \rangle$ values refer to the orthogonalized one-electron functions used by Tomiie & Stam (1958), and the approximation $\langle r^2 \rangle_{3s} = \langle r^2 \rangle_{3p}$ is the same as that involved in their f-curve derivation. The values of $\langle r^2 \rangle$ from the poly-detor wave functions of Boys & Price (1954) for Cl and S and of Bernal & Boys (1952) for Ne, as well as the corresponding $\langle r^2 \rangle$ for the 'root functions', were obtained during the derivation of the poly-detor f-curves (Dawson, 1960; 1961). Experimental estimates of mean square radii $\langle r^2 \rangle_{\text{exp.}}$ for Ne, A and Kr are also given in Table 1, and were obtained (see Ibers, 1958) from values of molar diamagnetic susceptibility (Kittel, 1956).

In Fig. 1, we plot the Hartree–Fock and Slater function values in Table 1(*A*) for $\langle r^2 \rangle_{\text{neon core}}$, $\langle r^2 \rangle_{3s}$ and $\langle r^2 \rangle_{3p}$ of atoms with Z from 10 (Ne) to 19 (K), and use these to obtain the smooth curves A, B and C.

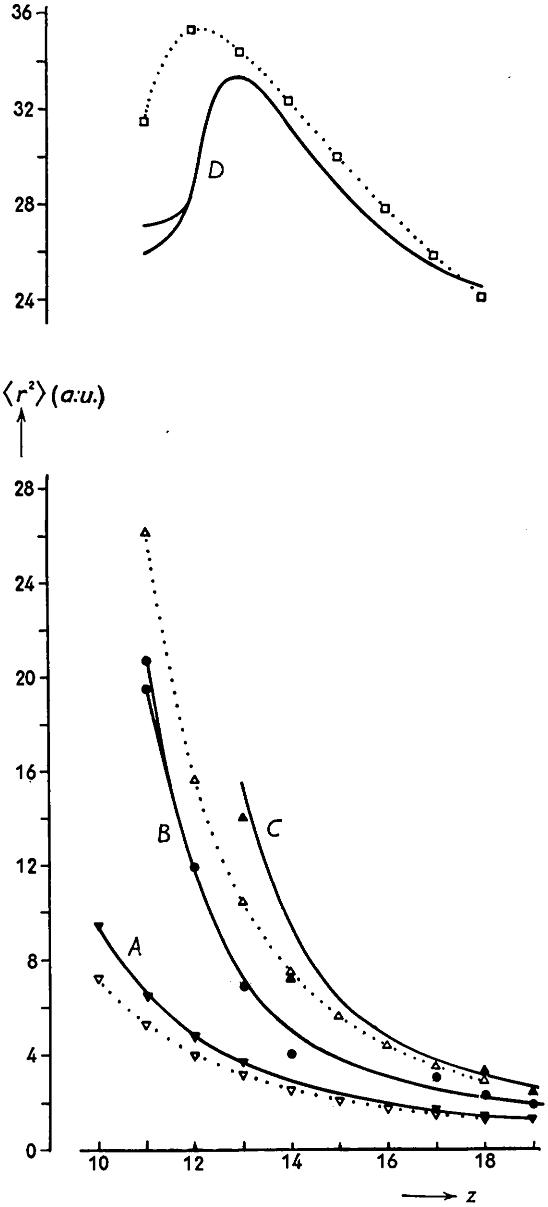

Fig. 1. The Hartree–Fock values of $\langle r^2 \rangle_{\text{neon core}}$, ▼; $\langle r^2 \rangle_{3s}$, ●; and $\langle r^2 \rangle_{3p}$, ▲; and the Slater function values of $\langle r^2 \rangle_{\text{neon core}}$, ▽; and $\langle r^2 \rangle_{3p,3s}$, △; used in obtaining curves A, B and C. The values of $\langle r^2 \rangle_{\text{total}}$ for Slater functions are □, and curve D is the corresponding result obtained from A, B, and C.

The values of $\langle r^2 \rangle$ for neutral atoms derived from these curves are given in Table 1(*B*).

In deriving these values, little uncertainty is involved for curve A, since changes in the Hartree–Fock values of $\langle r^2 \rangle_{\text{neon core}}$ with changes in state of ionization will be negligible for these atoms (see Hartree & Hartree, 1938*b*). For curves B and C, however, the uncertainties regarding variation of $\langle r^2 \rangle$ with state of

Table 2. *Atomic scattering amplitudes for electrons in Å*

(Based on the rest-mass of the electron (Ibers, 1958))

$\sin\theta/\lambda$ (Å^{-1})	F	Ne	Na	Mg	Al	Si	P	S	Cl	A	K	Ca	Kr
0·00	1·81	1·61	4·79	5·04	5·88	5·52	5·08	4·73	4·48	4·33	9·11	9·99	6·92
0·05	1·77	1·59	4·21	4·60	5·32	5·10	4·78	4·54	4·35	4·24	—	8·72	6·71
0·10	1·69	1·52	2·97	3·59	4·14	4·26	4·18	4·08	4·01	3·97	5·43	6·39	6·10
0·15	1·55	1·42	2·11	2·63	3·07	3·34	3·45	3·50	3·53	3·55	—	4·54	5·32
0·20	1·38	1·30	1·59	1·94	2·27	2·54	2·75	2·90	2·99	3·03	3·15	3·40	4·51
0·25	1·21	1·17	1·29	1·50	1·72	1·95	2·16	2·33	2·47	2·52	—	2·69	3·77
0·30	1·05	1·04	1·09	1·21	1·35	1·52	1·70	1·87	2·01	2·07	2·14	2·20	3·16
0·35	0·91	0·92	0·95	1·01	1·10	1·22	1·36	1·50	1·63	1·71	—	1·84	2·66
0·40	0·78	0·81	0·83	0·87	0·93	1·01	1·11	1·22	1·34	1·42	1·49	1·55	2·27
0·50	0·59	0·62	0·64	0·67	0·70	0·74	0·79	0·86	0·93	1·00	1·07	1·12	1·71
0·60	0·45	0·48	0·51	0·53	0·55	0·58	0·60	0·64	0·69	0·74	0·79	0·84	1·34
0·70	0·34	0·38	0·40	0·43	0·44	0·46	0·49	0·51	0·54	0·57	0·61	0·65	1·09
0·80	0·27	0·30	0·33	0·35	0·37	0·38	0·40	0·42	0·44	0·46	0·49	0·52	0·90
0·90	0·22	0·24	0·27	0·29	0·30	0·32	0·33	0·35	0·37	0·38	0·40	0·42	0·75
1·00	0·18	0·20	0·22	0·24	0·26	0·27	0·28	0·30	0·31	0·32	0·34	0·35	0·64

ionization are greater, and in using the Hartree–Fock data of Table 1(*A*), the following considerations were employed.

(i) With unit change in state of ionization, the radial changes in outer *s*- and *p*-electron charge distributions are greater for *p*-electrons, and the distributions for negative ions are more extended, and those for positive ions more contracted, than those of neutral atoms (see Hartree, Hartree & Swirles, 1939).

(ii) The Hartree–Fock results obtained by Biermann and co-workers using a polarization correction (Hartree, 1957) are considerably contracted as compared with results obtained by the normal Hartree–Fock procedure (see Table 1(*A*), $\langle r^2\rangle_{3p}$ values for K and Na).

(iii) Some contraction in normal Hartree–Fock results for outer electron distributions must be expected in view of the neglect of electron correlation effects other than exchange (Dawson, 1961). In this regard we have the poly-detor and Hartree–Fock values for Ne in Table 1(*A*) and also the fact that the Hartree–Fock $\langle r^2\rangle$ values there for A and Kr are larger than the $\langle r^2\rangle_{\text{exp.}}$ suggested by diamagnetic susceptibilities.

(iv) The poly-detor results for Cl in Table 1(*A*) are a useful guide to (iii) above since, with the 'root function' $\langle r^2\rangle$ value larger than that of the final poly-detor function, no uncertainties arise regarding effects concerned with radial limitations of the elementary set employed in the poly-detor calculations (see Dawson, 1960, 1961). For S, on the other hand, where the 'root function' $\langle r^2\rangle$ is smaller than that of the complete calculation, uncertainty regarding the radial limitations prevents the poly-detor value for this atom from being used in assessment of (iii).

(v) Although the smooth variation of $\langle r^2\rangle$ values of outer electrons with change of atomic number implied by the use of curves *B* and *C* is not strictly correct,[*] errors in the values of Table 1(*B*) arising from this assumption should not be of any great consequence.

In terms of these considerations, the values of $\langle r^2\rangle_{\text{total}}$ in Table 1(*B*) for A, Cl, S and possibly P should be fairly reliable. For Si and Al, however, the uncertainty is somewhat greater, since $\langle r^2\rangle_{3p}$ changes rapidly over this range of atomic number, and we have arbitrarily started curve *C* at $\langle r^2\rangle_{3p}=15{\cdot}5$, for Al, in view of (ii) above. This value for Al is smaller than that of the 3*p* function used by Freeman (1959*a*) for this atom,[†] but this is consistent with the fact that the values of $\langle r^2\rangle_{3p}$ for the other atoms in Table 1(*B*) are also smaller than those from normal Hartree–Fock calculations in view of (iii) above. Curve *D* of Fig. 1 shows the values of $\langle r^2\rangle_{\text{total}}$ of Table 1(*B*) for the atoms Al to A, and values for Na and Mg from Table 1(*A*). The smaller of the two values for Na is more in accord with the data used in obtaining the value for Mg (see Table 1(*A*)), although we have used the larger value for $f_{\text{el.}}(0)$ below. For comparison with curve *D*, Fig. 1 also shows the values for these atoms obtained from Slater functions.

The values of $f_{\text{el}}\cdot(0)$ obtained with equation (3) for all atoms in Table 1 are given in Table 2. Apart from the use of the values of $\langle r^2\rangle$ in curve *D* for the atoms noted above, the normal Hartree–Fock results for F, K, Ca and Kr, and the poly-detor result for Ne, have been used for Table 2. For $f_{\text{el.}}(s)$ values obtained with equation (2), the *f*-curve tables of Berghuis *et al.* (1955), Ibers (1958), Freeman (1959*b*, 1960), Worsley (1959) and Dawson (1960, 1961) were used directly for all atoms except Al, Si, P, S and A. For these latter, the values of $f_{\text{el.}}(s)$ in Table 2 were obtained by relating the $f_{\text{el.}}$ values given by Tomiie & Stam's (1958) Slater function *f*-values to curves similar to curve *D* in Fig. 1. For an example of the details as-

---

[*] For example, the values of $\langle r_2\rangle_{3d}$ for transition metals (Dawson, unpublished) obtained from Watson's (1959) Hartree–Fock calculations for the $(3d)^n$ configurations of lowest energy show only small variations from a smooth curve.

[†] Freeman's f_{3p} value for $\sin\theta/\lambda=0{\cdot}1$ Å^{-1} is 0·2650, while the corresponding value from Biermann & Lübeck's (1948) function (for which $\langle r^2\rangle_{3p}=14{\cdot}00$, Table 1(*A*)) is 0·3607. We estimate that the $\langle r^2\rangle$ value of Freeman's function is probably about 17.

sociated with this procedure see Vainshtein & Ibers (1958).

Comparison of the new values of $f_{el.}$ with the earlier results of Ibers (1958) and Vainshtein & Ibers (1958) shows that there are considerable differences when s is zero or small. This is the region where the values of $f_{el.}(s)$ are most sensitive to the charge distributions or f-curves used in their derivation. For F and Ne, the new values are some 10% lower than the earlier results, and this lowering satisfactorily removes the anomaly for these atoms noted by Ibers (1958). The greatest difference between new and earlier results is found for Kr, where the new results are again lower, this time by about 15%. For the other atoms, the new values are again lower than the earlier results, except for Al. For certain atoms where the present work employs the same Hartree–Fock charge density data as that used by Ibers (1958), namely for Na, Mg, A and Ca, there is some disparity between the values of $f_{el}(0)$ obtained for the Hartree–Fock results in Table 1(A), and the values of $f_{el\cdot}(0)$ given by Ibers (1958). It is presumed that these differences must have arisen from the integration procedure employed in the earlier work.

The author wishes to thank Dr A. J. Freeman for his kindness in providing a copy of Allen's (1957) results for F.

References

ALLEN, L. C. (1957). *Quarterly Progress Report, Solid State and Molecular Theory Group*, M.I.T., July 15, p. 62. (Unpublished.)

BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.

BERNAL, M. J. M. & BOYS, S. F. (1952). *Phil. Trans.* A, **245**, 139.

BIERMANN, L. & LÜBECK, K. (1948). *Z. Astrophys.* **25**, 325.

BIERMANN, L. & TREFFTZ, E. (1949). *Z. Astrophys.* **26**, 213.

BOYS, S. F. & PRICE, V. E. (1954). *Phil. Trans.* A, **246**, 451.

COWLEY, J. M. & REES, A. L. G. (1958). *Reports on Progress in Physics*. **21**, 165.

DAWSON, B. (1960). *Acta Cryst.* **13**, 403.

DAWSON, B. (1961). *Acta Cryst.* **14**, 1117.

FREEMAN, A. J. (1959*a*). *Phys. Rev.* **113**, 176.

FREEMAN, A. J. (1959*b*). *Acta Cryst.* **12**, 261.

FREEMAN, A. J. (1960). *Acta Cryst.* **13**, 190.

FROESE, C. (1957). *Proc. Camb. Phil. Soc.* **53**, 206.

HARTREE, D. R. (1957). *The Calculation of Atomic Structures*. New York: Wiley.

HARTREE, D. R. & HARTREE, W. (1936). *Proc. Roy. Soc.* A, **156**, 45.

HARTREE, D. R. & HARTREE, W. (1938*a*). *Proc. Roy. Soc.* A, **166**, 450.

HARTREE, D. R. & HARTREE, W. (1938*b*). *Proc. Camb. Phil. Soc.* **34**, 550.

HARTREE, D. R. & HARTREE, W. (1938*c*). *Proc. Roy. Soc.* A, **164**, 167.

HARTREE, D. R. & HARTREE, W. (1948). *Proc. Roy. Soc.* A, **193**, 299.

HARTREE, D. R., HARTREE, W. & SWIRLES, B. (1939). *Phil. Trans.* A, **238**, 229.

HARTREE, D. R., HARTREE, W. & MANNING, M. F. (1941). *Phys. Rev.* **60**, 857.

IBERS, J. A. (1958). *Acta Cryst.* **11**, 178.

JOST, W. J. (1940). *Phys. Rev.* **58**, 557.

KITTEL, C. (1956). *Introduction to Solid State Physics*. New York: Wiley.

SLATER, J. C. (1930). *Phys. Rev.* **36**, 87.

TOMIIE, Y. & STAM, C. H. (1958). *Acta Cryst.* **11**, 126.

VAINSHTEIN, B. K. & IBERS, J. A. (1958). *Soviet Physics-Crystallography*, **3**, 417.

WATSON, R. E. (1959). *Technical Report No. 12, Solid State and Molecular Theory Group*, M.I.T. (Unpublished.)

WORSLEY, B. H. (1958*a*). *Canad. J. Phys.* **36**, 289.

WORSLEY, B. H. (1958*b*). *Proc. Roy. Soc.* A, **247**, 390.

WORSLEY, B. H. (1959). *Canad. J. Phys.* **37**, 967.