Acta Cryst. (1967). **22**, 153

The relativistic Hartree–Fock X-ray and electron form factorsf or mercury.

By P.A.Doyle and P.S.Turner,
School of Physics, University of Melbourne, Australia

(*Received* 30 *June* 1966)

X-ray and electron form factors for mercury have been calculated from relativistic Hartree–Fock atomic fields. A brief comparison of f curves based on various atomic models is given. Significant differences are found between those based on the Slater exchange approximation, and the more accurate Fock method.

The relativistic Hartree–Fock (R–HF) atomic wave functions have been obtained by Coulthard (1966), who solved the equations given by Grant (1961), but with the magnetic terms and off-diagonal Lagrange parameters omitted. The effect of neglecting magnetic terms is expected to be very small, while for atoms such as mercury which consist entirely of closed groups of electrons the off-diagonal parameters are not required at all. From the wave functions, he has found atomic potentials $\varphi(r)$ and total charge densities $\varrho(r)$ at about 180 points r' from the nucleus given by $r'=\exp(T/16)/1370$ Bohr radii, where $T=-3, -2, -1, 0, 1, 2\ldots$.

Kinematic scattering factors for X-rays and electrons, $f_X(s)$ and $f_{el}(s)$, have been found from these using the equations

$$f_X(s)=\int_0^\infty 4\pi r^2 \varrho(r)\frac{\sin(4\pi sr)}{(4\pi sr)}\,dr$$

and

$$f_{el}(s)=\frac{8\pi^2 m_0 e}{h^2}\int_0^\infty r^2\varphi(r)\frac{\sin(4\pi sr)}{(4\pi sr)}\,dr$$

where $s=\sin\theta/\lambda$ Å^{-1} and r is in Å.

These are related by

$$f_{el}(s)=0{\cdot}023934\frac{Z-f_X(s)}{s^2}$$

where Z is the atomic number.

The results for mercury are presented in Table 1.

Table 1. *Relativistic Hartree–Fock form factors for mercury*

$\sin\theta/\lambda$ (Å^{-1})	$f_X(s)$ (electrons)	$f_{el}(s)$* (Å)	$\sin\theta/\lambda$ (Å^{-1})	$f_X(s)$ (electrons)	$f_{el}(s)$* (Å)
0·00	80·00	10·96	0·50	47·60	3·10
0·05	78·90	10·55	0·60	42·83	2·47
0·10	76·02	9·53	0·70	38·75	2·02
0·15	72·20	8·30	0·80	35·18	1·68
0·20	68·09	7·13	0·90	31·98	1·42
0·25	64·03	6·12	1·00	29·11	1·22
0·30	60·18	5·27	1·10	26·55	1·06
0·35	56·60	4·57	1·20	24·30	0·93
0·40	53·32	3·99	1·30	22·35	0·82
0·45	50·33	3·51	1·40	20·69	0·72

* These values must be multiplied by $m/m_0=(1-v^2/c^2)^{-\frac{1}{2}}$ for electrons of velocity v.

A comparison of f_X curves obtained from TFD, H, DS and HFS (non-relativistic Hartree with Slater exchange) calculations has been made by Cromer (1965). However, the influence on the f curves of the various atomic models is illustrated more clearly by examining those for electrons. Table 2 gives such a comparison. The first three columns show that the contraction of the outer electron shells resulting from exchange is overestimated by the Slater approximation. This is consistent with the fact that the R–HF eigenvalue for the 6*s* state in mercury (the outermost state) is 0·6566 Rydberg units, which is considerably lower than the Dirac–Slater value of 0·6974 obtained by Liberman,

Table 2. *Electron form factors for mercury* (Å)

	Self-consistent field calculations				
$\frac{\sin\theta}{\lambda}$	(1) Present R–HF	(2) DS	(3) RH	(4) H	(5) TFD
0·00	10·96	(10·3)	12·96	(14·0)	13·0
0·05	10·55	9·77	12·26	13·21	12·54
0·1	9·53	8·93	10·82	11·32	11·23
0·2	7·13	6·85	7·70	7·79	7·98
0·5	3·10	3·07	3·16	3·20	3·22
0·8	1·68	1·67	1·70	1·71	1·72
1·2	0·93	0·92	0·93	0·94	0·93

DS Dirac–Slater, from the $f_X(s)$ values of Cromer & Waber (1965). (Relativistic Hartree with Slater exchange).
RH Relativistic Hartree, from the atomic fields of Cohen (1960) or of Schonfelder (1966). (Relativistic Hartree without exchange).
H Hartree – from the $f_X(s)$ values of Cromer, Larson & Waber (1964). (Hartree field without relativity or exchange).
TFD Thomas–Fermi–Dirac model.
( ) Extrapolated values.

Waber & Cromer (1965). As pointed out by Ibers (1958), the approximate agreement between the relativistic Hartree and Thomas–Fermi–Dirac (TFD) f curves must be considered fortuitous. The alteration to the curves due to the inclusion of relativity is seen by comparing columns (3) and (4); that due to the more accurate inclusion of exchange is seen by comparing the present results in column (1) with column (2). From these, it appears that the present correction is comparable to the relativistic correction, so that the need for form factors for electrons, and for X-rays, based on the R–HF calculations is apparent. Therefore, we hope to publish a table of kinematic scattering factors, for both X-rays and electrons, including those for some ions, as the new wave functions become available.

We would like to thank Mr M.A.Coulthard for several helpful discussions, and for allowing us to use his as yet unpublished results.

References

Cohen, S. (1960). *Phys. Rev.* **118**, 489.
Coulthard, M. A. (1966). To be submitted for publication.
Cromer, D. T. (1965). *Acta Cryst.* **19**, 224.
Cromer, D. T., Larson, A. C. & Waber, J. T. (1964). *Acta Cryst.* **17**, 1044.
Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104.
Grant, I. P. (1961). *Proc. Roy. Soc.* A, **262**, 555.
Ibers, J. A. (1958). *Acta Cryst.* **11**, 447.
Liberman, D., Waber, J. T. & Cromer, D. T. (1965). *Phys. Rev.* **137**A, A27.
Schonfelder, J. L. (1966). *Proc. Phys. Soc.* **87**, 163.