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The relativistic X-ray form factor for mercury.

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The almost complete unavailability of wave functions based on the relativistic model has necessitated in X-ray studies the use of form factors uncorrected for relativistic effects. In this note we compute the form factor for mercury from both the non-relativistic and the recently calculated relativistic radial wave functions in order to determine the magnitude of the error in the form factor which results from the neglect of the effects of relativity.

The non-relativistic wave functions used were those obtained by Hartree & Hartree (1935) from the approximation of the self-consistent field without exchange. The relativistic wave functions used were those obtained by Cohen (1957) from the same approximation based on the relativistic wave equation. That is each of the electrons in the atom is assumed to satisfy the single-particle Dirac equation in the combined Coulombic fields from the nucleus and from the other electrons of the atom. In this way corrections are applied for those relativistic effects which arise from the variation of mass with velocity, and for those which in non-relativistic terms are ascribed to spin-orbit interaction. A more complete description of the relativistic extension is given by Hartree (1957) and also by Mayers (1957) who recently tabulated relativistic wave functions for mercury. Here we use the results of Cohen rather than those of Mayers, for the latter are less accurate.

The calculation of form factors from the radial wave functions has been described previously (Hoerni & Ibers, 1954; Berghuis *et al.*, 1955) and so here we note only that the intervals in r (in atomic units) employed were

$$0{\cdot}000(0{\cdot}005)0{\cdot}300;\quad 0{\cdot}30(0{\cdot}05)4{\cdot}00;\quad 4{\cdot}0(0{\cdot}5)9{\cdot}0.$$

Table 1. *X-ray form factors for mercury (in electrons)*

	Self-consistent field*		Statistical model	
$(\sin\theta)/\lambda$	Relativistic	Non-relativistic	TFD†	TF‡
0·00	80·00	80·00	80·00	80·0
0·05	78·72	78·63	78·69	—
0·10	75·48	75·30	75·31	74·6
0·15	71·37	71·23	70·99	—
0·20	67·14	67·04	66·66	65·9
0·25	63·09	62·96	62·62	—
0·30	59·31	59·12	58·84	57·9
0·35	55·84	55·56	55·30	—
0·40	52·65	52·31	52·06	51·1
0·50	47·04	46·69	46·40	45·6
0·60	42·31	42·01	41·59	40·9
0·70	38·22	37·97	37·54	36·8
0·80	34·64	34·40	34·06	33·4
0·90	31·43	31·15	31·08	30·5
1·00	28·59	28·24	28·50	28·0
1·10	26·07	25·63	26·25	25·9
1·20	23·88	23·35	24·27	24·0
1·30	21·99	21·41	22·52	22·4

* The second decimal places here are probably not significant, but are given as an aid to interpolation.

† These values are from Thomas & Umeda (1957).

‡ These values were obtained by interpolation between the values given by Umeda & Tomishima (1955).

Table 1 gives the values of f for mercury obtained here from the relativistic and non-relativistic* self-consistent fields and obtained previously from the Thomas–Fermi–Dirac (TFD) and Thomas–Fermi (TF) statistical models. A comparison of the form factors derived from the relativistic and non-relativistic self-consistent fields indicates that within the range of scattering of interest in X-ray analyses the neglect of relativity has a very minor effect on the form factor for mercury; presumably this is also true for other heavy atoms. The small effect which is found is at the high values of $(\sin\theta)/\lambda$ where the contributions to f of the inner electron shells are relatively greater: The inner shells are the ones most seriously affected by the relativistic corrections.

The difference between the form factor derived from the TFD model and that derived from the TF model is a measure of the effects of electron exchange, for the TFD model in effect includes corrections for electron exchange whereas the TF model does not. It can be seen from Table 1 that the effects on the derived form factors of electron exchange are generally greater than are those of relativity. If we assume that the effects of electron exchange are approximately the same for the self-consistent field approximation as for the statistical approximation, then the excellent agreement of the form factor derived from the TFD model with those derived from the self-consistent fields must be in part fortuitous. Nevertheless, from Table 1 it appears that form factors for atoms as heavy as mercury when based on the TFD model are sufficiently reliable for even the most careful X-ray investigations.

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* Although James (1948) plots f based on the self-consistent field versus $(\sin\theta)/\lambda$ for mercury no values of f appear to be tabulated in the literature.