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Calculation of the Electron Distribution in the Hydrogen Atom for Different Values of the Temperature Factor

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Tables are presented showing the effect of thermal vibration on the electron distribution in the hydrogen atom, both in three dimensions and in projection. The calculations, which were performed on the EDSAC, are based upon the assumption that the charge density in a stationary atom is adequately represented by the square of the normalised (1*s*) wave-function. In the three-dimensional case, $\varrho(r)$, the electron density in a vibrating atom, and $n(R)$, the fraction of the electron contained within a sphere of radius R measured from the centre of the atom, can be expressed explicitly as functions of the temperature parameter B. It is found that the atom is quite diffuse, a sphere of radius 1·0 Å, for example, containing only about 70% of the electron. In view of this, due care must be taken in interpreting the results of electron counting on electron-density maps computed from X-ray diffraction data. The magnitudes of the errors introduced by termination of the Fourier series are also discussed.

The results of these calculations agree reasonably well with recent measurements of the electron density. We conclude tentatively that the electron distribution in hydrogen atoms bonded to carbon, nitrogen or oxygen, or weakly hydrogen-bonded to nitrogen or chlorine, is adequately approximated by the electron distribution in an isolated atom.

Introduction

In a recent publication, Higgs (1953) has discussed the effect of thermal vibration upon the electron distribution in the carbon atom, and has demonstrated the very critical nature of the dependence of the peak density on the amplitude of thermal vibration, especially at low temperatures. In the present paper, it is proposed to investigate the effect of thermal motion on the electron distribution in the hydrogen atom. In view of the fact that the technique of X-ray diffraction has advanced to the stage where it is possible to measure the electron density in hydrogen atoms with fair accuracy, it is of some importance to know what values to expect under different experimental conditions.

We shall assume in what follows that the charge density in a stationary atom is adequately represented by the square of the normalised (1*s*) wave-function, that is, we shall ignore the perturbations of the electron cloud due to bonding. Justification for this apparently drastic simplification is afforded by recent experimental results. It is well known that the electron distribution in heavier atoms is relatively little affected by bonding, the departures from spherical symmetry being in general very small (apart from the effects of anisotropic thermal vibration). Recent accurate X-ray diffraction results suggest that this may also be true in the least favourable case of the hydrogen atom. It has been generally found (Table 9) that, if a spherically symmetrical distribution of electron density is subtracted from X in a covalent bond H–X by the technique of the F_o-F_c synthesis, the resultant distribution has, on the average, spherical symmetry, and

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the peak height and electron content are not very different from the values expected for an isolated atom calculated on the basis of the theory developed in this paper. This point will be discussed later with particular reference to Table 9.

While the deficiences of this simple approach are fully realized, the assumptions involved are valid to the extent that they form a genuine basis for the interpretation of the experimental results.

Three-dimensional analysis

For any spherically symmetrical atom, the number of electrons $n(R)$ contained within a sphere of radius R measured from the centre of the atom is given by

$$n(R) = \int_0^R 4\pi r^2 \varrho(r)\,dr = \int_0^R U(r)\,dr\,, \tag{1}$$

where $\varrho(r)$ is the electron density at a distance r from the centre. $U(r) = 4\pi r^2 \varrho(r)$ is the radial distribution function. For an atom with thermal motion, we have for $\varrho(r)$,

$$\varrho(r) = \int_{v^*} f(s) \exp(-Bs^2) \exp(-2\pi i \mathbf{r}\cdot\mathbf{s})\,dv^*\,, \tag{2}$$

where $f(s)$ is the atomic scattering factor, and $s = 2 \sin \theta/\lambda$. B is a constant related to the amplitude of thermal vibration:

$$B = 2\pi^2 \overline{u^2}\,,$$

where $\overline{u^2}$ is the mean square displacement of the atom from its mean position.

Equation (2) is normally evaluated as a Fourier series:

$$\varrho(x, y, z) = \frac{1}{V} \sum_h \sum_k \sum_l f(hkl) \exp(-Bs^2) \times \exp\{-2\pi i(hx+ky+lz)\}\,. \tag{3}$$

In the case of the hydrogen atom, $\varrho(r)$ is given in analytical form as the square of the normalized wavefunction. For a stationary atom in the ground state,

$$\varrho(r) = \psi^2(r) = (1/\pi a^3) \exp(-2r/a),\ a = 0{\cdot}528\ \text{Å}\,. \tag{4}$$

We shall assume that this also gives the electron density in an atom at absolute zero, though this will not be strictly true on account of the existence of zero-point energy. This point does not affect the analysis which follows, but in the comparison of observed and calculated densities (Table 9) it may be that the values of B which have been used, which are those appropriate to carbon atoms etc., should in fact be greater because of the greater zero-point movement of the hydrogen atoms.

The distribution function is, in this case,

$$U(r) = 4\pi r^2 \psi^2(r) = (4r^2/a^3) \exp(-2r/a)\,, \tag{5}$$

and the fraction of the electron within a sphere of radius R is

$$n(R) = \frac{4}{a^3}\int_0^R r^2 \exp(-2r/a)\,dr;$$

i.e.

$$n(R) = 1-(2/a^2)\,[R^2+aR+\tfrac{1}{2}a^2] \exp(-2R/a)\,. \tag{6}$$

The electron density in an atom with thermal motion will be obtained by convoluting (4) with the Fourier transform of the temperature function $\exp(-Bs^2)$. The transform is

$$T(r) = \int_0^\infty 4\pi s^2 \frac{\sin 2\pi rs}{2\pi rs} \exp(-Bs^2)\,ds\,,$$

i.e.

$$T(r) = (\pi/B)^{\frac{3}{2}} \exp(-\pi^2 r^2/B)\,. \tag{7}$$

Convoluting (7) with (4), we have

$$\begin{aligned}\varrho(u) &= \widehat{\psi^2(r)\,.\,T(r)} \\ &= \frac{1}{\pi a^3}\left(\frac{\pi}{B}\right)^{\frac{3}{2}} \int_v \exp\left(-\frac{2r}{a}\right) \exp\left\{-\frac{\pi^2}{B}\,|\mathbf{u}-\mathbf{r}|^2\right\} dv\,.\end{aligned}$$

Transforming to spherical polar coordinates, with the polar axis along $\mathbf{u}$, and using the spherical symmetry of the functions,

$$\begin{aligned}\varrho(u) = \frac{2}{a^3}\left(\frac{\pi}{B}\right)^{\frac{3}{2}} \exp\left(-\frac{\pi^2 u^2}{B}\right) \int_0^\infty \int_0^\pi r^2 \sin\alpha \\ \times \exp\left(-\frac{\pi^2 r^2}{B} + \frac{2\pi^2 ru}{B}\cos\alpha - \frac{2r}{a}\right) dr\,d\alpha\,.\end{aligned}$$

Integrating first with respect to α,

$$\begin{aligned}\varrho(u) = \frac{2 \exp(-\pi^2 u^2/B)}{\sqrt{(B\pi)}\,a^3 u} \\ \times \int_0^\infty r \exp\left(-\frac{\pi^2 r^2}{B} - \frac{2r}{a}\right) \sinh\left(\frac{2\pi^2 ru}{B}\right) dr\,.\end{aligned}$$

Replacing u by r, we have finally for the modified density,

$$2\pi a^3 r \varrho(r) = F(r) - F(-r)\,, \tag{8}$$

where

$$F(r) = \left(\frac{B}{a\pi^2} + r\right)\left[1 - \operatorname{erf}\left(\frac{\sqrt{B}}{a\pi} + \frac{\pi r}{\sqrt{B}}\right)\right] \exp\left(\frac{B}{\pi^2 a^2} + \frac{2r}{a}\right)\,,$$

with the convention that

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}}\int_0^x \exp(-y^2)\,dy = -\operatorname{erf}(-x)\,.$$

Equation (8) gives the electron density in a hydrogen atom with a temperature factor of $\exp[-B(2\sin\theta)^2/\lambda^2]$. On putting $B = 0$, the expression reduces to (4). The fraction of the electron inside a sphere of radius R can be obtained by graphical integration of the area under the distribution function of (8), or by exact integration. The integration has been accomplished, with the following result:

$$n(R) = G(R)-G(-R)+\operatorname{erf}\left(\frac{\pi R}{\sqrt{B}}\right)-\frac{2\sqrt{B}}{a^2\pi^{\frac{3}{2}}}R\exp\left(-\frac{\pi^2R^2}{B}\right),$$

where

$$G(R) = \frac{1}{a^2}\left[R^2+R\left(\frac{B}{a\pi^2}-a\right)-\tfrac{1}{2}a\left(\frac{B}{a\pi^2}-a\right)\right]$$
$$\times\left[1-\operatorname{erf}\left(\frac{\pi R}{\sqrt{B}}+\frac{\sqrt{B}}{a\pi}\right)\right]\exp\left(\frac{2R}{a}+\frac{B}{\pi^2a^2}\right).$$

This may be simplified by making the approximations

$$\operatorname{erf}(\pm\pi R/\sqrt{B}+\sqrt{B}/a\pi)=\pm1, \quad\text{and}\quad \exp(-\pi^2R^2/B)=0,$$

which give rise to a small error for the values of B and R which we are interested in, and lead to the rather neat result

$$n(R) = 1-\frac{2}{a^2}\left[R^2-R\left(\frac{B}{a\pi^2}-a\right)-\tfrac{1}{2}a\left(\frac{B}{a\pi^2}-a\right)\right]$$
$$\times\exp\left(-\frac{2R}{a}+\frac{B}{a^2\pi^2}\right), \quad (9)$$

which reduces to (6) on putting $B = 0$.

Equation (8) may also be derived from the atomic scattering factor,

$$f(s) = \frac{4}{a^3}\int_0^\infty r^2\frac{\sin 2\pi rs}{2\pi rs}\exp\left(-\frac{2r}{a}\right)dr,$$

i.e.

$$f(s) = 1/[1+(\pi as)^2]^2. \quad (10)$$

This is the scattering amplitude for the ground state of the hydrogen atom at absolute zero. McWeeny (1951) finds that the contribution of the (1s) orbital to the atomic scattering factor is given by

$$f(1s) = (N_{1s})^2\left(\frac{\pi}{2\mu^3a^3}\right)\frac{S_1(x)}{x},$$

where

$$S_1(x) = \int_0^\infty te^{-t}\sin xt\,dt = \frac{2x}{(1+x^2)^2}.$$

Substituting $x = \pi as$, $(N_{1s})^2 = \mu^3a^3/\pi$, we obtain (10).

For an atom in thermal vibration, we have for the electron density:

$$\varrho(r) = \int_0^\infty \frac{4\pi s^2}{[1+(\pi as)^2]^2}\,\frac{\sin 2\pi rs}{2\pi rs}\exp(-Bs^2)ds. \quad (11)$$

Table 1. *The three-dimensional electron density as a function of the temperature parameter B and the distance r from the centre of the atom*

(Values are in e.Å^{-3})

r(Å) \ B(Å^2)	0·00	0·25	0·50	0·75	1·00	1·25	1·50
0·0	2·162	$1{\cdot}14_0$*	$0{\cdot}89_1$*	$0{\cdot}74_5$*	$0{\cdot}64_5$*	$0{\cdot}57_1$*	$0{\cdot}51_7$*
0·1	1·481	1·054	0·847	0·715	0·622	0·551	0·495
0·2	1·014	0·856	0·728	0·633	0·561	0·504	0·457
0·3	0·694	0·639	0·578	0·523	0·475	0·435	0·400
0·4	0·475	0·458	0·435	0·408	0·382	0·357	0·335
0·5	0·325	0·322	0·315	0·306	0·294	0·281	0·269
0·6	0·223	0·224	0·224	0·223	0·219	0·214	0·208
0·7	0·153	0·156	0·158	0·159	0·159	0·159	0·157

* Calculated for $r = 0{\cdot}01$ by equation (8).

Table 2. *The three-dimensional distribution function* $4\pi r^2\varrho(r)$

r(Å) \ B(Å^2)	0·00	0·25	0·50	0·75	1·00	1·25	1·50
0·0	0·000	0·000	0·000	0·000	0·000	0·000	0·000
0·1	0·186	0·133	0·106	0·090	0·078	0·069	0·062
0·2	0·510	0·430	0·366	0·318	0·282	0·253	0·230
0·3	0·785	0·723	0·654	0·591	0·538	0·492	0·453
0·4	0·956	0·921	0·874	0·821	0·768	0·719	0·673
0·5	1·022	1·012	0·991	0·960	0·923	0·884	0·845
0·6	1·008	1·016	1·015	1·007	0·991	0·969	0·943
0·7	0·939	0·958	0·972	0·980	0·982	0·977	0·968
0·8	0·840	0·865	0·887	0·905	0·919	0·928	0·932
0·9	0·728	0·755	0·780	0·803	0·824	0·841	0·855
1·0	0·615	0·642	0·667	0·692	0·715	0·737	0·756
1·1	0·510	0·534	0·558	0·582	0·605	0·628	0·649
1·2	0·415	0·437	0·458	0·480	0·502	0·523	0·545
1·3	0·334	0·352	0·371	0·390	0·409	0·429	0·448
1·4	0·265	0·280	0·296	0·312	0·329	0·346	0·363
1·5	0·208	0·221	0·234	0·247	0·261	0·276	0·290
1·6	0·162	0·172	0·183	0·194	0·205	0·217	0·230
1·7	0·125	0·134	0·142	0·151	0·160	0·170	0·180
1·8	0·096	0·103	0·109	0·116	0·124	0·131	0·140
1·9	0·073	0·078	0·084	0·089	0·095	0·101	0·108
2·0	0·056	0·060	0·064	0·068	0·072	0·077	0·082

Table 3. *The fraction of the electron n(R) contained within a sphere of radius R as a function of R and B*

R(Å) \ B(Å^2)	0·00	0·25	0·50	0·75	1·00	1·25	1·50
0·7	0·49	0·47	0·45	0·43	0·41	0·39	0·37
0·8	0·58	0·56	0·54	0·52	0·50	0·49	0·47
0·9	0·66	0·64	0·63	0·61	0·59	0·57	0·55
1·0	0·73	0·71	0·70	0·68	0·67	0·65	0·64
1·1	0·78	0·77	0·76	0·75	0·73	0·72	0·71
1·2	0·83	0·82	0·81	0·80	0·79	0·78	0·77
1·3	0·87	0·86	0·85	0·84	0·83	0·82	0·81
1·4	0·90	0·89	0·88	0·88	0·87	0·86	0·85
1·6	0·94	0·94	0·93	0·93	0·92	0·92	0·91
1·8	0·97	0·96	0·96	0·96	0·96	0·95	0·95
2·0	0·98	0·98	0·98	0·98	0·97	0·97	0·97

Integration of this expression leads to equation (8). The values of the electron density in three dimensions were first calculated by means of equation (8), and the results were later checked by numerical integration of (11) on the EDSAC (Table 1). Using the result

$$\int_0^\infty \exp(-pt)\sin(a\sqrt{t})dt = \frac{a}{2p}\sqrt{\left(\frac{\pi}{p}\right)}\exp\left(-\frac{a^2}{4p}\right),$$

we can write equation (11) in the form of a differential equation

$$\left(1-\pi^2a^2\frac{\partial}{\partial B}\right)^2\varrho(r) = \left(\frac{\pi}{B}\right)^{\frac{3}{2}}\exp\left(-\frac{\pi^2r^2}{B}\right), \quad (11a)$$

which is suitable for numerical evaluation on the machine.

Effect of series termination

The values of $\varrho(r)$ and $n(R)$ obtained by the use of these equations strictly apply only to Fourier syntheses which have been computed with an infinite number of terms. This is not the case in practice, of course, and the measured values will depend to a certain extent upon the limit of the observations, the error being greater the smaller the value of B. We must therefore enquire under what conditions the results of the present calculations are applicable. A rigorous treatment will not be attempted; the problem may conveniently be tackled by considering the effect of series termination upon the peak electron density. The peak density $\varrho(0)_A$ corresponding to termination at $s = A$ is given by

$$\varrho(0)_A = 4\pi \int_0^A \frac{s^2}{[1+(\pi a s)^2]^2} \exp(-Bs^2)\,ds\,. \qquad (12)$$

This integral is intractable, but results sufficiently accurate for the present purpose may be obtained by numerical integration. The values of $\varrho(0)_A$ for different limits A are given in Table 4. They are expressed as fractions of the peak values given in Table 1. It is seen that the reduction in peak density is quite appreciable for normal values of B, and in general, in three dimensions, a correction will be necessary. These figures represent maximum corrections, in the sense that the corrections to $\varrho(r)$ are invariably less than to $\varrho(0)$. The effect of series termination upon $n(R)$ is more difficult to assess with accuracy, but it is less than in the case of $\varrho(r)$, and the values in Table 3 can probably be used with confidence for normal experimental conditions.

Table 4. *The effect of series termination on the peak electron density $\varrho(0)$ in three dimensions*

($\varrho(0_A)$ is expressed as a fraction of the values in Table 1)

B(Å^2) / A(Å^{-1})	0·25	0·50	0·75	1·00	1·25	1·50
1·0	0·64	0·74	0·81	0·85	0·89	0·92
1·1	0·69	0·79	0·85	0·89	0·93	0·95
1·2	0·74	0·84	0·89	0·92	0·95	0·97
1·3	0·79	0·87	0·92	0·95	0·97	0·98
1·4	0·82	0·90	0·95	0·97	0·98	0·99
1·5	0·85	0·93	0·96	0·98	0·99	
1·6	0·88	0·95	0·98	0·99		
1·7	0·90	0·96	0·99			

Two-dimensional analysis

The extension of the above treatment to two dimensions has not been found possible, owing to the intractable nature of the integrals. The projected electron density in a hydrogen atom with thermal motion is

$$\varrho(r) = \int_0^\infty \frac{2\pi s}{[1+(\pi a s)^2]^2} \exp(-Bs^2) J_0(2\pi r s)\,ds\,, \qquad (13)$$

where J_0 denotes the Bessel function of order zero.

For the special case $B = 0$, we have from (4),

$$[\varrho(r)]_{B=0} = \frac{2}{\pi a^3} \int_0^\infty \exp\left[-\frac{2}{a}(r^2+h^2)^{\frac{1}{2}}\right] dh\,,$$

which can be rewritten

$$[\varrho(r)]_{B=0} = \frac{4}{\pi a^4} \int_r^\infty (s^2-r^2)^{\frac{1}{2}} \exp\left(-\frac{2s}{a}\right) ds\,,$$

and, using the result

$$\int_0^\infty f(t) \exp(-pt)\,dt = \frac{a}{p} K_1(ap)\,,$$

where $f(t) = (t^2-a^2)^{\frac{1}{2}}$ for $t > a$, and $f(t) = 0$ for $t < a$, we have for the projected electron density

$$[\varrho(r)]_{B=0} = \frac{2}{\pi a^3} r K_1\left(\frac{2r}{a}\right)\,. \qquad (13a)$$

Table 5. *The projected electron density as a function of the temperature parameter B and the distance r from the centre of the atom*

(Values are in e.Å^{-2})

B(Å^2) / r(Å)	0·00	0·25	0·50	0·75	1·00	1·25	1·50
0·0	1·142	0·92$_5$*	0·81$_8$*	0·74$_2$*	0·68$_3$*	0·63$_6$*	0·59$_6$*
0·1	1·009	0·875	0·785	0·717	0·663	0·619	0·582
0·2	0·809	0·752	0·696	0·648	0·607	0·572	0·541
0·3	0·624	0·604	0·579	0·552	0·527	0·503	0·481
0·4	0·470	0·467	0·459	0·449	0·436	0·423	0·410
0·5	0·348	0·352	0·353	0·352	0·348	0·343	0·338
0·6	0·255	0·261	0·265	0·268	0·270	0·270	0·269
0·7	0·186	0·191	0·197	0·201	0·205	0·207	0·209

* Calculated by means of equation (16).

Table 6. *The two-dimensional distribution function $2\pi r\varrho(r)$*

B(Å^2) / r(Å)	0·00	0·25	0·50	0·75	1·00	1·25	1·50
0·0	0·000	0·000	0·000	0·000	0·000	0·000	0·000
0·1	0·634	0·550	0·493	0·451	0·417	0 389	0·365
0·2	1·017	0·945	0·874	0·814	0·763	0·719	0·680
0·3	1·176	1·139	1·091	1·041	0·993	0·948	0·907
0·4	1·180	1·173	1·154	1·127	1·097	1·064	1·032
0·5	1·094	1·105	1·109	1·104	1·094	1·079	1·061
0·6	0·962	0·983	1·000	1·012	1·017	1·018	1·015
0·7	0·816	0·841	0·864	0·884	0·900	0·912	0·920
0·8	0·674	0·699	0·724	0·747	0·768	0·786	0·801
0·9	0·544	0·568	0·592	0·615	0·636	0·657	0·676
1·0	0·433	0·454	0·475	0·496	0·516	0·536	0·556
1·1	0·339	0·357	0·375	0·393	0·412	0·430	0·448
1·2	0·263	0·278	0·293	0·308	0·324	0·340	0·355
1·3	0·202	0·214	0·226	0·239	0·252	0·265	0·278
1·4	0·154	0·163	0·173	0·183	0·194	0·204	0·216
1·5	0·116	0·124	0·131	0·139	0·148	0·156	0·165
1·6	0·087	0·093	0·099	0·105	0·112	0·118	0·125
1·7	0·065	0·070	0·074	0·079	0·084	0·089	0·095
1·8	0·049	0·052	0·055	0·059	0·063	0·067	0·071
1·9	0·036	0·038	0·041	0·044	0·047	0·050	0·053
2·0	0·026	0·028	0·030	0·032	0·035	0·037	0·039

K_1 is a well tabulated function (see for example Watson, 1922, p. 698). The values in column 1 of Tables 5 and 6 were calculated by means of this equation. Equation (13) can be written in the form of a convergent series, but, as the functions involved are not well tabulated, the series is not convenient for accurate calculation. The remaining columns in Tables 5 and 6 were obtained on the EDSAC as the solutions of the differential equation

$$\left(1-\pi^2a^2\frac{\partial}{\partial B}\right)^2\varrho(r)=\left(\frac{\pi}{B}\right)\exp\left(-\frac{\pi^2r^2}{B}\right), \tag{14}$$

which can be obtained from (13) by using the result

$$\int_0^\infty \exp\left(-pt\right)J_0(2\sqrt{(at)})\,dt=\frac{1}{p}\exp\left(-\frac{a}{p}\right).$$

In two dimensions, $n(R)$ is given by

$$n(R)=\int_0^R 2\pi r\varrho(r)\,dr\,. \tag{15}$$

Table 7 was obtained by graphical evaluation of this function.

Table 7. *The fraction of the electron $n(R)$ contained within a circle of radius R as a function of R and B*

B(Å²) / R(Å)	0·00	0·25	0·50	0·75	1·00	1·25	1·50
0·7	0·65	0·63	0·62	0·60	0·58	0·57	0·55
0·8	0·72	0·71	0·70	0·68	0·67	0·65	0·64
0·9	0·78	0·77	0·76	0·75	0·74	0·73	0·71
1·0	0·83	0·82	0·81	0·80	0·79	0·78	0·77
1·1	0·87	0·86	0·86	0·85	0·84	0·83	0·82
1·2	0·90	0·89	0·89	0·88	0·88	0·87	0·86
1·3	0·92	0·92	0·92	0·91	0·91	0·90	0·89
1·4	0·94	0·94	0·94	0·93	0·93	0·92	0·92
1·6	0·96	0·96	0·96	0·96	0·96	0·96	0·95
1·8	0·98	0·98	0·98	0·98	0·98	0·97	0·97
2·0	0·99	0·98	0·98	0·98	0·98	0·98	0·98

We can derive an analytical expression for the effect of temperature on the peak electron density. In two dimensions, $\varrho(0)$ is

$$\varrho(0)=\int_0^\infty \frac{2\pi s}{[1+(\pi as)^2]^2}\exp\left(-Bs^2\right)ds\,,$$

which can be reduced to a tabulated form

$$\varrho(0)=\frac{1}{\pi a^2}[1+be^bEi(-b)]\,, \tag{16}$$

where

$$-Ei(-b)=\int_b^\infty \frac{e^{-t}}{t}\,dt \quad \text{(Jahnke \& Emde, 1945, p. 1)}$$

and $b=B/a^2\pi^2$.

The effect of series termination may be conveniently discussed in terms of this equation. For a finite upper limit A, equation (16) becomes

$$\varrho(0)_A=\varrho(0)-\left(\frac{b}{\pi a^2}\right)e^bEi[-(b+BA^2)] -\frac{b}{\pi a^2}\frac{\exp\left(-BA^2\right)}{b+BA^2}\,. \tag{17}$$

The magnitude of the error introduced by limiting the series may readily be determined for any particular values of A and B by evaluating the two correction terms. Table 8 was obtained in this way. The figures have the same significance as those in Table 4. As is to be expected, they impose less stringent restrictions upon the experimental conditions than is the case in three dimensions.

Table 8. *The effect of series termination on the peak electron density $\varrho(0)$ in two dimensions*

($\varrho(0)_A$ is expressed as a fraction of the values in Table 5)

B(Å²) / A(Å⁻¹)	0·25	0·50	0·75	1·00	1·25	1·50
1·0	0·85	0·89	0·92	0·94	0·96	0·97
1·1	0·88	0·92	0·95	0·96	0·97	0·98
1·2	0·90	0·94	0·96	0·97	0·98	0·99
1·3	0·92	0·96	0·97	0·98	0·99	
1·4	0·94	0·97	0·98	0·99		
1·5	0·95	0·98	0·99			
1·6	0·96	0·98				
1·7	0·97	0·99				

Numerical results

Values of $\varrho(r)$ calculated on the EDSAC are listed in Tables 1 and 5, for several values of B, and for $r \leqslant 0·7$ Å. $\varrho(r)$ plotted as a function of r is shown in Fig. 1. The effect of thermal motion is to lower the electron density for $r < \sim 0·5$ Å, and to increase it slightly outside this range. In three dimensions, from equation (8),

$$\left(\frac{\partial\varrho}{\partial B}\right)_{B=0}=\frac{1}{\pi^3a^5}\left(1-\frac{a}{r}\right)\exp\left(-\frac{2r}{a}\right).$$

This function changes sign when $r=a$, thus the effect of a small temperature increase on a stationary atom in three dimensions is to decrease ϱ for $r < 0·528$ Å, and to increase ϱ for $r > 0·528$ Å. In two dimensions, from equation (13),

$$\left[\frac{\partial\varrho}{\partial B}\right]_{B=0}=\frac{2}{\pi^3a^4}\left[\frac{r}{a}K_1\left(\frac{2r}{a}\right)-K_0\left(\frac{2r}{a}\right)\right].$$

This function is zero when $r=aK_0(2r/a)/K_1(2r/a)$, that is when $r=0·41$ Å. Thus, in two dimensions, the electron density is decreased by thermal motion for $r < 0·41$ Å, and increased beyond this value, for an atom near the absolute zero of temperature. The latter effect is rather too small to be shown in Fig. 1, and is best brought out by the change in the radial distribution function. $U(r)$ is tabulated in Tables 2 and 6 for r ranging from 0 to 2·0 Å, and the corresponding curves for $B = 0$ and $B = 1{\cdot}50$ are plotted in Fig. 2. Thermal motion has the effect of displacing the maxima of the distribution curves in an outward direction, and lowering them slightly.

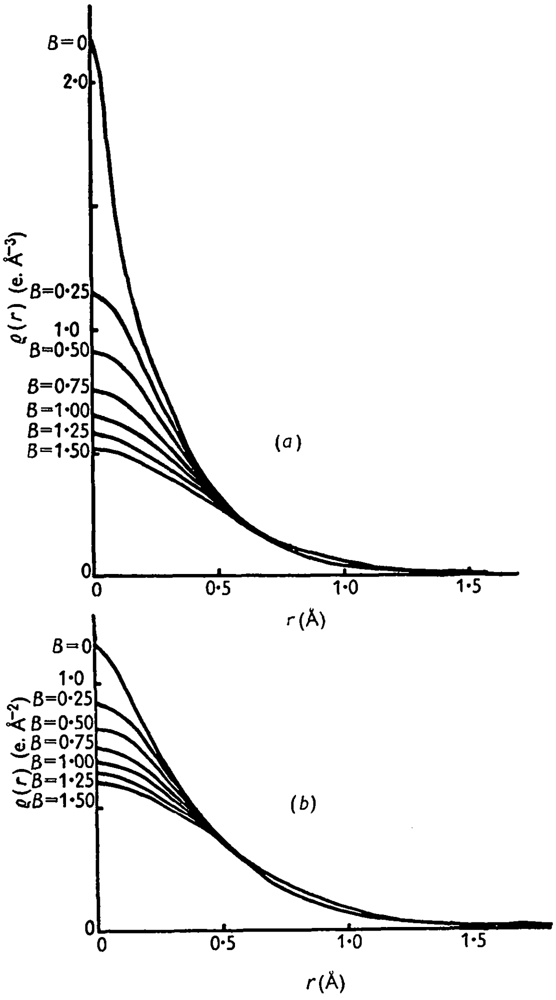

Fig. 1. The electron density (*a*) in three dimensions, (*b*) in two dimensions, as a function of r and B.

Tables 3 and 7 list $n(R)$ for $0{\cdot}7\ \text{Å} \leqslant R \leqslant 2{\cdot}0\ \text{Å}$. The values in Table 3 were obtained from equation (9), and those in Table 7 from equation (15). It can be seen that the atom is quite diffuse, a sphere of radius 1·0 Å, for example, containing only 70% of the electron. The values of $n(R)$ are relatively little affected by temperature.

Conclusion

In Table 9 a comparison is made between the theoretical calculations and the results of recent accurate analyses of salicylic acid (Cochran, 1953), adenine hydrochloride (Cochran, 1951), α-pyridone (Penfold, 1953), ammonium bifluoride (McDonald, 1956) and α-phenazine (Hirshfeld & Schmidt, 1956). The values of $\varrho_o(0)$ and $n_o(R)$ in the table are as read on $\varrho_o - \varrho_c$ maps computed from Geiger-counter data in the case of the first four structures, and from low-temperature (90° K.) photographic data in the case of α-phenazine. The values of B and R which were used in the calculations are indicated in the table. B is, in each case, an average temperature factor for the whole molecule. The $\varrho_o(0)$ values for ammonium bifluoride were corrected for series-termination effects, but this refinement was not necessary for the other analyses.

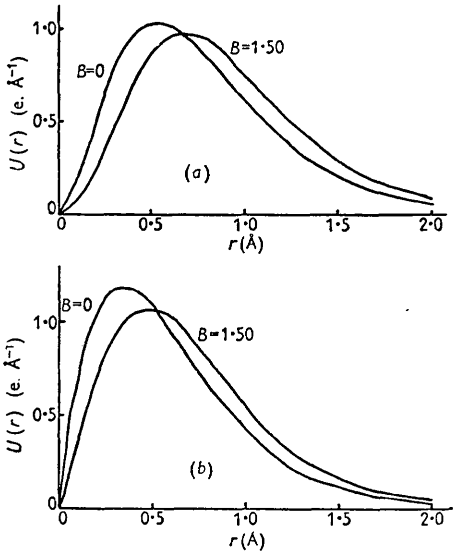

Fig. 2. The distribution function (*a*) $U(r) = 4\pi r^2 \varrho(r)$ and (*b*) $U(r) = 2\pi r \varrho(r)$, for $B = 0$ and $B = 1{\cdot}50$.

The hydrogen atoms taking part in the formation of the strong O–H–O bonds in salicylic acid and F–H–F bonds in ammonium bifluoride have been excluded from the table, the reason being that they appeared abnormal. In salicylic acid, these hydrogen atoms are deficient as regards both peak density and electron content, while in ammonium bifluoride, although the electron count is normal, the peak densities are low. Similar effects have been observed by Pringle (1954) in oxalic acid dihydrate.

The following points are worthy of note in respect of Table 9. It is not unreasonable to suppose that bonding would, if anything, reduce the electron content of the hydrogen atom, but, apart from the exceptions mentioned in the preceding paragraph, there is no indication of any such deficiency in either $\varrho_o(0)$ or $n_o(R)$ as compared with $\varrho_c(0)$ and $n_c(R)$. In fact, there is a slight tendency for the experimental peak densities to be higher than the theoretical, as though the hydrogen atoms, contrary to expectation, had smaller average thermal vibrations than the heavy atoms.

The tentative conclusion to be drawn from this comparison is that the electron distribution in hy-

Table 9. *Comparison of observed and calculated values of* $\varrho(0)$ *and* $n(R)$

	$\varrho_o(0)$ (e.Å^{-2})	$\varrho_c(0)$ (e.Å^{-2})	$n_o(R)$ (e)	$n_c(R)$ (e)	B (Å^2)	R (Å)
Salicylic acid	0·81	0·68	0·95	0·84	1·00	1·1
	0·79	—	0·91	—	—	—
	0·79	—	0·86	—	—	—
	0·71	—	0·97	—	—	—
Adenine hydrochloride	1·07	0·78	0·81*	0·85	0·59	1·1
	1·00	—	—	—	—	—
	0·70	—	—	—	—	—
	1·07	—	—	—	—	—
	0·87	—	—	—	—	—
	0·72	—	—	—	—	—
	1·00	—	—	—	—	—
α-Phenazine†	1·11	0·89	0·8*	0·70	0·32	0·8
	1·23	—	—	—	—	—
	0·95	—	—	—	—	—
	0·93	—	—	—	—	—
α-Pyridone	0·80	0·77	0·95	0·80	0·65	1·0
	0·78	—	0·89	—	—	—
	0·80	—	0·94	—	—	—
	0·70	—	0·94	—	—	—
	0·78	—	0·91	—	—	—
Ammonium bifluoride	0·92‡	0·83‡	0·79	0·75	0·59	1·1
	0·96‡	—	0·79	—	—	—

* Averaged over all the atoms. † Preliminary results. ‡ Values in units e.Å^{-3}.

drogen atoms bonded to carbon, nitrogen or oxygen, or weakly hydrogen-bonded to nitrogen or chlorine, is adequately approximated by the distribution in an isolated atom.

Finally we must bear in mind the following practical considerations. If we wish to detect departures from the electron content of an isolated atom, we must count within a region small compared with interatomic distances, that is, R should not exceed about 1·0 Å. Under these conditions, as can be seen from the tables, the expected electron count is considerably less than one. In view of this, it is evident that due care must be taken in interpreting the results of electron counting on Fourier syntheses, particularly in three-dimensional work. In two dimensions, the situation may be worse as regards overlap, but is better from the point of view of sharpness of the peaks. In either case, we must endeavour to strike a compromise in practice between trying to include the 'whole' atom, on the one hand, and avoiding the effects of overlap, on the other.

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