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Thomas-Fermi-Dirac Calculations of Incoherent-Scattering Factors[*]

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The incoherent-scattering factor (S) derivation of Heisenberg is extended to include the Thomas-Fermi-Dirac (TFD) model of the atom. TFD neutral-atom calculations of the electron densities and potentials are made with the use of a slope-iteration scheme. The calculations of S show that the TFD values of S are much smaller than the Thomas-Fermi values for small momentum transfers and, therefore, are in better agreement with Hartree-Fock values. The improvement is much greater for small-Z atoms. A comparison of Hartree-Fock and TFD S values is given over a wide range of momentum transfers for the rare gases.

I. INTRODUCTION

Inelastic (Compton) scattering of x rays from a free atom with Z electrons is often calculated by utilizing the free-atom incoherent-scattering factor $S(\vec{k})$ in the equation

$$\frac{d\sigma}{d\Omega} = ZS(\vec{k})\left(\frac{d\sigma}{d\Omega}\right)_{\mathrm{fr}}, \tag{1}$$

where

$$S(\vec{k}) = \frac{1}{Z}\left(\sum_{n,m=1}\langle\Psi_0|\,e^{i\vec{k}\cdot(\vec{r}_n-\vec{r}_m)}\,|\Psi_0\rangle - |F(\vec{k})|^2\right), \tag{2}$$

Ψ_0 is the ground state of the atom, and

$$F(\vec{k}) = \sum_n \langle\Psi_0|\,e^{i\vec{k}\cdot\vec{r}_n}\,|\Psi_0\rangle \tag{2a}$$

is the coherent-scattering factor.[1] The term $(d\sigma/d\Omega)_{\mathrm{fr}}$ represents the scattering cross section for a free electron at rest which at low incident photon energies is the Thomson cross section. Equations (1) and (2) can be derived from a nonrelativistic lowest-order Born-theory calculation (ignoring $\vec{p}\cdot\vec{A}$ terms) where a sum up to some highest energetically possible continuum state is replaced by a sum over all states[2] so that closure can be invoked. In addition, a term $(\omega_2/\omega_1)^2$, where ω_1 is the incident photon frequency and ω_2 is the scattered frequency, within the sum is set identically equal to 1.[3] At higher incident photon energies and/or large momentum transfers, $(d\sigma/d\Omega)_{\mathrm{fr}}$ is usually taken to be the Klein-Nishina scattering cross section. We note that no relativistic treatment from first principles has been performed to obtain this result. One observes that $S(\vec{k})$ is a monotonically increasing function going from 0 to 1 as k varies from 0 to ∞. Thus, the effect of binding is to reduce the inelastic scattering cross section below that resulting from Z independent free electrons at rest. In the forward direction the inelastic scattering cross section goes to zero, while at large momentum transfers $S(\vec{k})$ goes to 1 and we obtain scattering from free electrons as one expects physically.

The values of $S(\vec{k})$ have been previously calculated by utilizing numerical Hartree-Fock (HF)[4,5] wave functions for all atoms of the periodic table. These values are considered to be the most accurate calculations for all but the smallest atoms. Recently, many-parameter variational wave functions have been utilized to calculate $S(\vec{k})$ for two-, three-, and four-electron systems by Kim and Inokuti[6] and by Brown.[7,8] Their calculations have shown that $S(\vec{k})$ varies much more with the choice of ground-state wave function that does $F(\vec{k})$. This is not surprising since $S(\vec{k})$ depends on expectation values of two-electron operators. For He for $k \lesssim 0.5$ Å^{-1}, $S(\vec{k})$, calculated by using HF wave functions, lies about 5% above calculations which utilize many-parameter variational wave functions. In Be for $k \lesssim 0.1$ Å^{-1}, the HF $S(\vec{k})$ lies about 30% above the many-parameter configuration-interaction calculation.[8] This is consistent with the study of Dawson[9] who observed that the use of configuration-interaction wave functions which include electron correlation leads to charge distributions which are less extensive radially than those of the HF model. In larger atoms, many-parameter variational wave functions are not available. Therefore, our Thomas-Fermi-Dirac (TFD) $S(\vec{k})$ values are compared with HF results, and here the term "accurate" refers to agreement with the HF results. However, from the foregoing discussion one should bear in mind that for small momentum transfers

TABLE I. $-\chi$ (10^{-6} cm^3/mole).

	TF[a]	TFD[b]	HF	Expt.[c]
Ne	67.0	14.33	7.42	6.96 ± 0.14
Ar	81.0	22.13	20.62	19.32
Kr	102.0	35.48	31.3	29.00 ± 0.4
Xe	117.0	45.97	49.62	45.5 ± 0.7

[a] P. Gombás, *Die Statische Theorie des Atoms und ihre Anwendungen* (Springer-Verlag, Vienna, 1949), p. 233.

[b] Our results may differ from those in Ref. 13 by as much as 0.03 in the values shown.

[c] C. Barter *et al.*, J. Phys. Chem. 64, 1312 (1960).

the HS $S(\vec{k})$ values may themselves be inaccurate.

The TFD statistical model of the atom, which includes exchange effects omitted in the Thomas-Fermi (TF) model, has been discussed widely in the literature.[10-13] Thomas[14] has obtained solutions to the TFD equation by changing to a new dependent variable and numerically integrating in from the outer radius. Thomas and Umeda utilized the resulting electron density to calculate $F(k)$ (Ref. 15) and $\langle r^2\rangle$.[16] The expectation value $\langle r^2\rangle$ is simply related to the diamagnetic suspectibility χ of an atom by[17]

$$-\chi\,(\mathrm{cm}^3/\mathrm{mole}) = (0.791\,987\times 10^{-6})\langle r^2\rangle. \tag{3}$$

The values of $F(k)$ calculated in the TFD approximation can be observed to lie within a few percent of the HF calculated values for $k \lesssim 1.5$ Å^{-1} for all atoms of the Periodic Table. TFD values of $\langle r^2\rangle$ are much improved (smaller) than those calculated by using TF charge distribution. The TF charge density falls off as r^{-4} at large r rather than exponentially. Thus, the TF charge density is too smeared out at large r, and expectation values of operators which probe the outside of the atom such as $\langle r^2\rangle$ are much too large. The TFD electron density drops sharply to zero at some finite outer radius and therefore, one obtains substantially improved results for $\langle r^2\rangle$. Note that $\rho(r)$ calculated either in the TFD approximation or in the TF approximation diverges $\sim r^{-3/2}$ as $r\to 0$.[8] In Table I[18] we make a comparison of the HF[17] and our TFD calculated χ's and experiment in the rare gases. For purposes of completeness, we also include the TF values. In the special case of Xe one observes that the TFD $\langle r^2\rangle$ is closer to experiment for Xe than the HF $\langle r^2\rangle$. For spherically symmetric atoms at small k,

$$F(k) \sim Z - k^2\langle r^2\rangle/3! + O(k^4). \tag{4}$$

Therefore, if one has confidence in the experimental diamagnetic susceptibility of Xe, the TFD $F(k)$ values for small k will also be more accurate than the HF values of $F(k)$. This, of course, is fortuitous, and we imply no generalizations from the Xe case.

Bewilogua[19] has calculated a universal $S(w)$ curve (w is simply related to k) using the TF model and the theoretical treatment of Heisenberg.[20] Pohler and Hanson[21] have calculated a table of the Heisenberg-Bewilogua S function over a much smaller grid size than was obtained originally. For small k, the Heisenberg-Bewilogua S function lies far above the HF values for any atom. This is again a result of the smeared out TF charge distribution on the outside of the atom.

In the present paper we have extended the treatment of Heisenberg in order to calculate S in the TFD approximation. This is discussed in Sec. II. In so doing we have also modified an ion TFD code of Barnes[22] so that it applies to free atoms to obtain the TFD electron density and potential. We have performed these calculations primarily because they are of interest within the TFD model approach. Such statistical models giving accurate averages are of value in providing a clear concise description of the relevant physical phenomena. We also wanted to observe the extent to which $S(k)$ for small k is improved (decreased) from the TF result, since the TFD charge density is much less diffuse than the TF density. We give TFD results for S for the rare gases to Xe and also for Hg. Comparisons are made with HF and TF calculations. We note that a recent calculation utilizing a modified TF statistical model to calculate S has been performed by Singh.[23] In Singh's approach the experimental values of the diamagnetic susceptibility were utilized to obtain the electron charge density parameters.

II. TFD CALCULATION

The TFD nonlinear differential equation can be written

$$\frac{d^2\phi}{dx^2} = x\left[\left(\frac{\phi}{x}\right)^{1/2} + \beta\right]^3, \tag{5}$$

where

$$\beta = \left(\frac{b}{a_0 Z}\right)\frac{1}{\pi\sqrt{2}},$$

$$b = \frac{(3\pi)^{2/3}}{2^{7/3}}\,a_0 Z^{-1/3},$$

and a_0 is the Bohr radius. In terms of the usual radial coordinate r potential energy $V(r)$, r is equal to xb and

$$V(r) = -\frac{Ze^2}{r}\,\phi + \frac{e^2}{a_0}\,\frac{1}{2\pi^2}. \tag{6}$$

In terms of x, the electron density $\rho(x)$ is

$$\rho(x) = \frac{1}{3a_0^3\pi^5\beta^3}\left[\left(\frac{\phi}{x}\right)^{1/2} + \beta\right]^3 \tag{7a}$$

TABLE II. $ZS(k)$ for the rare gases.

	Neon		Argon		Krypton		Xenon	
k(Å^{-1})	TFD	HF[a]	TFD	HF[a]	TFD	HF[a]	TFD	HF[a]
0.005	0.136	0.002	0.189	0.006	0.272	0.009	0.333	0.013
0.010	0.272	0.009	0.378	0.024	0.544	0.035	0.667	0.052
0.050	1.349	0.218	1.876	0.571	2.703	0.812	3.312	1.194
0.100	2.612	0.812	3.650	1.956	5.288	2.703	6.494	3.841
0.150	3.621	1.637	5.127	3.588	7.522	4.805	9.300	6.677
0.200	4.416	2.547	6.346	5.033	9.446	6.760	11.763	9.340
0.300	5.621	4.269	8.292	7.377	12.670	10.157	15.987	13.892
0.400	6.489	5.644	9.785	8.998	15.291	12.828	19.516	17.307
0.500	7.139	6.640	10.969	10.106	17.479	14.969	22.533	20.175
0.600	7.640	7.320	11.928	10.967	19.337	16.849	25.152	22.833
0.700	8.033	7.774	12.719	11.726	20.936	18.562	27.451	25.324
0.800	8.347	8.085	13.378	12.424	22.325	20.123	29.489	27.619
0.900	8.599	8.312	13.933	13.061	23.542	21.535	31.307	29.680
1.000	8.806	8.490	14.406	13.629	24.616	22.804	32.938	31.488
1.500	9.418	9.113	15.953	15.489	28.477	27.313	39.072	37.628
2.000	9.686	9.517	16.751	16.324	30.802	29.870	43.040	41.477
3.000	9.888	9.875	17.465	17.132	33.284	32.659	47.661	46.254
4.000	9.951	9.967	17.737	17.573	34.454	33.919	50.084	49.030
5.000	9.975	9.991	17.857	17.800	35.061	34.562	51.459	50.673
8.000	9.994	10.000	17.965	17.978	35.723	35.504	53.144	52.591

[a] For $k \leq 1.5$ Å^{-1}, Hf results are taken from Ref. 1. For larger values of k, the HF values are taken from D. Cromer (private communication).

and the local Fermi momentum P_F is

$$P_F(x) = \frac{h}{2}\left(\frac{3}{\pi}\right)^{1/3} \rho^{1/3}(x) \quad . \tag{7b}$$

Equation (5) is solved by utilizing the boundary conditions

$$\phi(0) = 1 \, , \tag{8a}$$

$$\frac{\phi(x_0)}{x_0} = \frac{d\phi}{dx}\bigg|_{x_0} \quad \text{or} \quad \int_0^{x_0} \rho(x) x^2 \, dx = Z \, , \tag{8b}$$

where x_0 denotes the outer radius of the neutral TFD atom and

$$\phi(x_0)/x_0 = \beta^2/16 \, , \tag{8c}$$

which follows for a free atom (pressure equals 0 at $x = x_0$). Abrahamson[24] has shown that the latter boundary condition is equivalent to $\rho(x_0) = 0.002\,127/a_0^3$. Our numerical integration procedure consisted of putting in a value for x_0 (our results for x_0 agreed with Thomas to four and sometimes five significant figures and, therefore, Thomas values represented a very good starting point), putting in an estimated slope at the origin, and testing if ϕ goes negative before x_0 (which is unphysical since it would lead to complex electron densities). For ϕ remaining positive, the slope was iterated on until charge neutrality at $x = x_0$ was obtained. A further set of iterations to fulfill Eq. (8c) was then performed. We did not use the asymptotic series of Feynman, Metropolis, and Teller[25] at small values of x in our numerical integration procedures.

Heisenberg evaluated Eq. (2) for $S(k)$ for an antisymmetrized single-particle product wave function, the orbitals of which were plane waves with momentum values at any radial coordinate r ranging from 0 to $P_F(r)$, to obtain Eq. (20) in his work. This equation may be written

$$S = 1 - \frac{1}{Z}\left(\frac{8\pi}{3h^3}\right) \int_0^{r_1} dV \left(P_F(r) - \frac{kh}{4\pi}\right)^2 \left(P_F(r) + \frac{kh}{8\pi}\right) \, , \tag{9a}$$

with dV the spatial volume element and r_1 determined from

$$P_F(r_1) = kh/4\pi \, . \tag{9b}$$

To this point the derivation may apply to any local electron gas approximation, although his final result, Eq. (23) in his paper, is restricted to the TF atom. Thus, to obtain the TFD incoherent scattering factor, we transform to x and utilize Eqs. (7a) and (7b) with ϕ determined from Eq. (5), and obtain

$$S = 1 - \int_0^{x_1} dx \, x^2 \left[\left(\frac{\phi}{x}\right)^{1/2} + \beta - w\right]^2 \left[\left(\frac{\phi}{x}\right)^{1/2} + \beta + \frac{w}{2}\right] \, , \tag{10a}$$

where x_1 is determined from

$$\phi(x_1)/x_1 = (w - \beta)^2 \tag{10b}$$

for the case

$$(w - \beta) > \beta/4 \tag{10c}$$

and

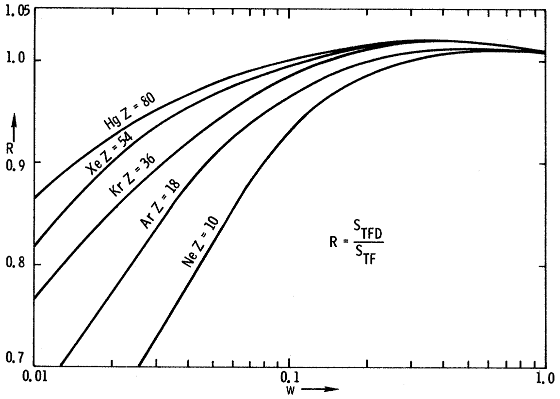

FIG. 1. Ratio R of S_{TFD}/S_{TF} as a function of w for Ne, Ar, Kr, Xe, and Hg.

$$x_1 = x_0 \qquad (10b')$$

for

$$(w - \beta) < \beta/4 . \qquad (10c')$$

In the above, $w = 2.21215k$ ($Å^{-1}$)$/Z^{2/3}$, with k ($Å^{-1}$) $=(1/\lambda)\sin\frac{1}{2}\theta$.

III. DISCUSSION OF RESULTS

In Table II we compare ZS_{TFD} with ZS_{HF} for the rare gases. We observe that although S_{TFD} values are much smaller than S_{TF} at small k, they still lie substantially higher than S_{HF}. At values of $k = 0.5$ $Å^{-1}$, the S_{TFD} results are larger than S_{HF} values by about 10%. Much closer agreement is found as we go to larger values of w. At very large momentum transfers ($k > 4$ $Å^{-1}$ for Ne), S_{TFD} becomes smaller than S_{HF}. This is related to the larger charge density (infinite) near the nucleus in the TFD atom.

In Fig. 1, we plot the ratio R of S_{TFD}/S_{TF} as a function of w for Ne, Ar, Kr, Xe, and Hg. For low atomic numbers, S_{TFD} is observed to be much smaller than S_{TF} at low momentum transfer (w). Thus, a considerable improvement over TF results is found in this region when TFD calculations are utilized. For $Z = 80$ where exchange effects are smaller, R remains much closer to 1 for small w. As w increases, R increases to 1 and then becomes greater than 1 by as much as 2% before decreasing back to 1 at large w.

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