

Atomic Scattering Factors of Helium-Like Systems from Analytic Hartree-Fock Wave Functions*

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The most widely used atomic scattering factors are based on numerical Hartree-Fock wave functions, some of which are of low accuracy. Recently a number of analytical Hartree-Fock functions have been published which have a higher accuracy than the older numerical wave functions. By using these analytical wave functions, there are obtained, in turn, analytical expressions for the scattering factors. These expressions can be readily evaluated at any desired interval of $\lambda^{-1} \sin \theta$ with a higher precision than can the numerically integrated scattering factors. The analytical Hartree-Fock scattering factors for the two-electron series to C^{+4} , including the previously unpublished values for H^{-} and refined values for He, Be^{+2} , and B^{+3} are reported here. In those cases where comparison is possible with recent carefully performed numerical Hartree-Fock calculations (Li^{+} and C^{+4}), the agreement is excellent.

Introduction

For many years, the most widely used atomic scattering factor values were those computed by James & Brindley (1931) who employed Hartree self-consistent field (SCF) wave functions. As Hartree obtained these numerical solutions without the benefit of present, improved computational techniques and facilities, their accuracy and hence the accuracy of the corresponding form factors are limited to fewer significant figures than may now be obtained. Moreover, because Hartree solutions were available to them for only a few atoms, James & Brindley (hereafter JB) resorted to an interpolation scheme to extend them to many others. Theoretical considerations (McWeeny, 1951; Hoerni & Ibers, 1954) as well as experimental evidence (Bacon, 1952; Cochran, 1953) have shown this interpolation procedure to be unreliable.

For these reasons, various efforts have been made to improve the old JB values. Thus, McWeeny, and more generally Freeman (1959) considered the effects of aspherical charge distributions on the scattering factor. In this laboratory, the effects of radial and angular correlation on the form factor have been investigated (Hurst, Miller & Matsen, 1958; Hurst & Matsen, 1959; Silverman, Platas & Matsen, 1960; Hurst, 1960). Several authors have used recent, more accurate SCF functions to extend and refine the old JB values (Viervoll & Øgrim, 1949; Hoerni & Ibers, 1954, 1957; Berghuis *et al.*, 1955; Freeman, 1959).

It appears, however, that for the two-electron iso-electronic series H^{-} - Ne^{+8} , form factors from improved numerical SCF functions have been reported only for Li^{+} and C^{+4} . Thus for He, Be^{+2} , B^{+3} and N^{+5} , the

only SCF form factors appearing in the literature are those of JB in which the He value was obtained from an early (Hartree, 1928) SCF function and the Be^{+2} , B^{+3} and N^{+5} values were found by their interpolation routine. SCF form factors for the remaining four members of the series appear not to have been previously reported.

Recently, analytical SCF functions for the helium-like systems have become available. Green *et al.* (1954) and more elaborately, Roothaan, Sachs & Weiss (1960) have developed analytic expressions closely approximating Hartree-Fock (HF) $1s$ wave functions in $1s^2$ configurations.†

In the present paper, an analytic expression for the atomic form factors of He and the helium-like ions is obtained from these analytic SCF functions. Using this expression, previously unreported SCF atomic form factors of H^{-} , O^{+6} , F^{+7} and Ne^{+8} are calculated as well as refined values of He, Be^{+2} , B^{+3} and N^{+5} . For Li^{+} and C^{+4} , comparison of the form factors given here with those calculated from accurate numerical SCF functions should indicate how well the analytic functions approximate the numerical Hartree-Fock functions for form factor calculations.

Calculations

The scattering factors are computed from (see James, 1948)

$$f = \int \Psi^* \sum_j \exp [ikS \cdot r_j] \Psi d\tau / \int \Psi^* \Psi d\tau, \quad (1a)$$

where

$$kS \cdot r_j = \mu r_j \cos \alpha_j \quad (1b)$$

$$\mu = 4\pi\lambda^{-1} \sin \theta \quad (1c)$$

$$d\tau = d\tau_1 d\tau_2 \quad (1d)$$

$$d\tau_j = r_j^2 dr_j \sin \alpha_j d\alpha_j d\varphi_j. \quad (1e)$$

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† The latter authors also report analytical SCF functions for the $1s^2 2s$ and $1s^2 2s^2$ atomic configurations.

Table 1. *Scattering factors computed from analytical SCF wave functions*

$\lambda^{-1} \sin \theta$ (\AA^{-1})	H ⁻	He	Li ⁺	Be ⁺²	B ⁺³	C ⁺⁴
0.000	2.0000	2.0000	2.0000	2.0000	2.0000	2.0000
0.025	1.9191	1.9891	1.9959	1.9979	1.9987	1.9991
0.050	1.7113	1.9572	1.9837	1.9915	1.9948	1.9965
0.075	1.4495	1.9057	1.9636	1.9809	1.9883	1.9921
0.100	1.1931	1.8373	1.9360	1.9663	1.9793	1.9860
0.125	0.9702	1.7551	1.9015	1.9477	1.9677	1.9781
0.150	0.7866	1.6626	1.8606	1.9254	1.9538	1.9686
0.175	0.6388	1.5633	1.8140	1.8995	1.9375	1.9575
0.200	0.5205	1.4602	1.7625	1.8703	1.9190	1.9448
0.225	0.4258	1.3563	1.7068	1.8380	1.8983	1.9305
0.250	0.3500	1.2538	1.6479	1.8030	1.8756	1.9147
0.275	0.2889	1.1545	1.5865	1.7655	1.8510	1.8975
0.300	0.2397	1.0598	1.5232	1.7258	1.8246	1.8790
0.325	0.1998	0.9704	1.4589	1.6842	1.7966	1.8591
0.350	0.1673	0.8868	1.3941	1.6410	1.7671	1.8380
0.375	0.1407	0.8094	1.3295	1.5965	1.7362	1.8158
0.400	0.1190	0.7380	1.2655	1.5509	1.7042	1.7925
0.425	0.1010	0.6726	1.2026	1.5047	1.6710	1.7681
0.450	0.08615	0.6128	1.1411	1.4579	1.6369	1.7429
0.475	0.07379	0.5584	1.0813	1.4109	1.6020	1.7168
0.500	0.06348	0.5089	1.0235	1.3638	1.5665	1.6900
0.550	0.04754	0.4233	0.9143	1.2705	1.4940	1.6343
0.600	0.03616	0.3530	0.8145	1.1791	1.4203	1.5764
0.650	0.02789	0.2954	0.7241	1.0910	1.3465	1.5171
0.700	0.02180	0.2482	0.6429	1.0068	1.2732	1.4568
0.750	0.01724	0.2093	0.5706	0.9271	1.2011	1.3960
0.800	0.01379	0.1773	0.5064	0.8522	1.1308	1.3352
0.850	0.01115	0.1509	0.4496	0.7823	1.0627	1.2749
0.900	0.009097	0.1289	0.3995	0.7175	0.9971	1.2154
0.950	0.007489	0.1106	0.3554	0.6576	0.9344	1.1570
1.000	0.006216	0.09523	0.3165	0.6024	0.8746	1.1000
1.100	0.004379	0.07149	0.2522	0.5053	0.7642	0.9909
1.200	0.003167	0.05448	0.2022	0.4242	0.6662	0.8894
1.300	0.002343	0.04210	0.1633	0.3567	0.5800	0.7961
1.400	0.001769	0.03296	0.1327	0.3007	0.5047	0.7112
1.500	0.001359	0.02611	0.1087	0.2543	0.4393	0.6346

Table 2. *Comparison of scattering factors computed from various wave functions*

$\lambda^{-1} \sin \theta$ (\AA^{-1})	0.00	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90	1.00	1.10	Wave function
H ⁻	2.000	1.193	0.520	0.240	0.119	0.0635	0.0362	0.0218	0.0138	0.0091	0.0062	0.0044	<i>G</i>
	2.000	1.185	0.517	0.247	0.126	0.0680	0.0390	0.0236	0.0150	0.0099	0.0068	0.0048	<i>HY</i>
	2.000	1.126	0.530	0.253	0.127	0.0677	0.0384	0.0230	0.0145	0.0095	0.0065	0.0046	<i>A</i>
He	2.000	1.837	1.460	1.060	0.738	0.509	0.353	0.248	0.177	0.129	0.0952	0.0715	<i>R</i>
	2.000	1.838	1.461	1.061	0.739	0.509	0.354	0.249	0.178	0.129	0.0953	0.0715	<i>HY</i>
	2.000	1.833	1.456	1.061	0.744	0.515	0.357	0.250	0.178	0.129	0.0945	0.0705	<i>A</i>
Li ⁺	2.000	1.936	1.762	1.523	1.266	1.023	0.814	0.643	0.506	0.400	0.317	0.252	<i>R</i>
	2.000	1.936	1.763	1.524	1.266	1.025	0.816	0.644	0.507	0.400	0.317	0.252	<i>HY</i>
	2.000	1.935	1.760	1.522	1.266	1.026	0.818	0.647	0.510	0.403	0.319	0.253	<i>A</i>
	2.000	1.936	1.762	1.522	1.264	1.022	0.813	0.642	0.505	0.398	0.316	0.252	<i>HF</i>
Be ⁺²	2.000	1.966	1.870	1.726	1.551	1.364	1.179	1.007	0.852	0.717	0.602	0.505	<i>R</i>
	2.000	1.966	1.870	1.726	1.551	1.364	1.180	1.008	0.853	0.719	0.603	0.506	<i>HY</i>
	2.000	1.966	1.869	1.725	1.550	1.364	1.180	1.009	0.855	0.721	0.606	0.508	<i>A</i>
B ⁺³	2.000	1.979	1.919	1.825	1.704	1.566	1.420	1.273	1.131	0.997	0.875	0.764	<i>R</i>
	2.000	1.979	1.919	1.825	1.704	1.567	1.421	1.274	1.132	0.998	0.876	0.765	<i>HY</i>
	2.000	1.979	1.919	1.824	1.703	1.566	1.420	1.274	1.132	0.999	0.877	0.767	<i>A</i>
C ⁺⁴	2.000	1.986	1.945	1.879	1.792	1.690	1.576	1.457	1.335	1.215	1.100	0.991	<i>R</i>
	2.000	1.986	1.945	1.879	1.792	1.690	1.577	1.457	1.336	1.216	1.101	0.992	<i>HY</i>
	2.000	1.986	1.945	1.879	1.792	1.689	1.576	1.457	1.335	1.216	1.101	0.992	<i>A</i>
	2.000	1.986	1.945	1.880	1.794	1.692	1.579	1.459	1.338	1.219	1.104	0.994	<i>HF</i>

R = Analytic SCF (Roothaan, Sachs & Weiss, 1960).*G* = Analytic SCF (Green *et al.*, 1954).*HY* = Three-term Hylleraas function (Hurst, 1960).*A* = Radially and angularly correlated (Silverman, Platas & Matsen, 1960).*HF* = Numerical SCF (Freeman, 1959).

The $1S$ normalized wave function used in the calculation is

$$\Psi = \varphi(1)\varphi(2), \quad (2a)$$

where the antisymmetric spin function has been omitted. The $\varphi(j)$ are the 'compromise'* SCF wave functions of Roothaan, Sachs & Weiss (1960) which may be written as

$$\varphi(j) = \alpha_0 1s(j) + \alpha_1 2s(j) + \beta_0 1s'(j) + \beta_1 2s'(j) \quad (2b)$$

where

$$1s(j) = (a^3/\pi)^{1/2} \exp[-ar_j] \quad (2c)$$

$$2s(j) = (a^5/3\pi)^{1/2} r_j \exp[-ar_j] \quad (2d)$$

$$1s'(j) = (b^3/\pi)^{1/2} \exp[-br_j] \quad (2e)$$

$$2s'(j) = (b^5/3\pi)^{1/2} r_j \exp[-br_j]. \quad (2f)$$

The parameters α_0 , α_1 , β_0 , β_1 , a and b have been determined by Roothaan *et al.* for He-Ne⁺⁸. The explicit expression for the scattering factor in modified atomic units† is

$$\begin{aligned} f = & \frac{32a^4}{(4a^2 + \mu^2)^2} \left[\alpha_0^2 + \frac{\alpha_0\alpha_1(12a^2 - \mu^2)}{(4a^2 + \mu^2)\sqrt{3}} + \frac{4\alpha_1^2 a^2(4a^2 - \mu^2)}{(4a^2 + \mu^2)^2} \right] \\ & + \frac{32b^4}{(4b^2 + \mu^2)^2} \left[\beta_0^2 + \frac{\beta_0\beta_1(12b^2 - \mu^2)}{(4b^2 + \mu^2)\sqrt{3}} + \frac{4\beta_1^2 b^2(4b^2 - \mu^2)}{(4b^2 + \mu^2)^2} \right] \\ & + \frac{32(ab)^{3/2}}{[(a+b)^2 + \mu^2]^2} \left\{ \alpha_0\beta_0(a+b) \right. \\ & + \frac{(a\alpha_1\beta_0 + b\alpha_0\beta_1)[3(a+b)^2 - \mu^2]}{[(a+b)^2 + \mu^2]\sqrt{3}} \\ & \left. + \frac{4\alpha_1\beta_1 ab(a+b)[(a+b)^2 - \mu^2]}{[(a+b)^2 + \mu^2]^2} \right\}. \quad (3) \end{aligned}$$

The scattering factors for He-Ne⁺⁸ were obtained from (3) using the parameter values computed by Roothaan *et al.* For $\alpha_1 = 0 = \beta_1$, $\alpha_0 = N(Z)^{-3/2}/2$, $\beta_0 = cN(kZ)^{-3/2}/2$, $a = Z$ and $b = kZ$, equation (2b) reduces to the three-parameter function of Green *et al.* while equation (3) reduces to the corresponding scattering expression; values of Z , k , c and N have been computed by Green *et al.* (1954) for H⁻-C⁺⁴. The scattering factor of H⁻ was obtained from this specialized form of (3) using the Green parameters. The calculations were performed on an IBM 650 computer.

* These functions represent a compromise between accuracy and complexity. Properties computed with these should differ but negligibly from values computed with the most elaborate functions given by these authors.

† The modified atomic unit of length, a_M , is given by $a_M = a_0(R_\infty/R_M)$ where $a_0 = 0.529172$ Å is the first Bohr radius for infinite nuclear mass, R_∞ is the Rydberg wave number for infinite nuclear mass and R_M is the Rydberg wave number for the nucleus of mass M . This introduces a first-order correction for nuclear motion.

Results

In Table 1 are given the form factors for H⁻, He, Li⁺, Be⁺², B⁺³ and C⁺⁴ for various values of $\lambda^{-1} \sin \theta^*$ in Å⁻¹. In Table 2 these results are compared with factors computed from other charge distributions.

Discussion

From Table 2 it is seen that the analytical SCF form factors are in good agreement with the results from both the three-term Hylleraas function and the radially and angularly correlated function of Silverman, Platas & Matsen. Furthermore, for Li⁺ and C⁺⁴ the analytical SCF form factors are in excellent agreement with those obtained from accurate numerical HF functions, showing maximum deviations of 0.002 and 0.004 electron for Li⁺ and C⁺⁴ respectively. Thus, for the form factor calculations of these ions, the analytic functions are excellent approximations to the numerical HF solutions. One can reasonably expect that the analytic functions for the other members of the series approximate their numerical counterparts to a like degree.

In view of the relative ease and high precision with which the scattering integral may be evaluated from analytic SCF functions at any desired interval of $\lambda^{-1} \sin \theta$, as opposed to evaluation from numerical ones, it seems preferable to compute form factors from them when such functions are available.

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* Tables of the factors for H⁻-Ne⁺⁸ for values of $\lambda^{-1} \sin \theta$ up to 20.0 Å⁻¹ will be supplied upon request.