

# Coherent and Incoherent X-Ray Scattering by Bound Electrons.

## II. Three- and Four-Electron Atoms\*

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Atomic form factors and incoherent-scattering functions for the lithium and beryllium isoelectronic sequences through  $Z=8$  have been calculated with correlated ground-state wave functions. The form factors differ from Hartree-Fock values by 1-2% and differ from Hartree-Slater values by as much as 10%. The incoherent-scattering functions are much more dependent on correlation, with the values for neutral beryllium differing from the Hartree-Fock values by as much as 30% at very small values of the momentum transfer.

### I. INTRODUCTION

This paper reports an extension to the lithium and beryllium isoelectronic sequences of earlier work,<sup>1</sup> hereafter referred to as I, on atomic scattering factors. The form factor for an  $N$ -electron atom or atomic ion, given by

$$F(K) = \sum_{j=1}^N \langle \psi_0 | e^{i\vec{K} \cdot \vec{r}_j} | \psi_0 \rangle, \quad (1)$$

and the incoherent-scattering function

$$S(K) = N^{-1} \left( \sum_{j,k=1}^N \langle \psi_0 | e^{i\vec{K} \cdot (\vec{r}_j - \vec{r}_k)} | \psi_0 \rangle - |F(K)|^2 \right) \quad (2)$$

contain the structure-dependent parts of the cross sections for coherent and incoherent x-ray scattering, respectively. The functions  $F(K)$  and  $S(K)$  also appear in the Born-approximation electron-atom scattering cross sections, and have several other applications in scattering theory.<sup>2</sup> In Eqs. (1) and (2) the momentum transfer is given by  $\hbar\vec{K}$ ,  $\vec{r}_j$  is the radius vector from the nucleus to the  $j$ th electron, and  $\psi_0$  is the ground-state wave function.

### II. METHOD

The wave functions used in the present work are the variational wave functions of Weiss.<sup>3</sup> These give ground-state energies which are considerably better than those obtained with Hartree-Fock or Hartree-Slater functions, and are comparable in accuracy<sup>4</sup> to those used in I for the helium isoelectronic sequence. Like those used in I, they are configuration-interaction expansions, but differ in that the single-particle functions are normalized Slater orbitals rather than products of angular-momentum eigenfunctions and Laguerre polynomials. This type of expansion has both advantages and disadvantages when compared with the expansion in denumerably complete polynomials, or Sturmian functions, used in I. One of the advantages is that the matrix elements are considerably easier to calculate, since the radial functions are

single powers of  $r$ . However, this simple form of the function requires that a large number of nonlinear variational parameters be used (9 for the lithium sequence and 11 for the beryllium sequence), and it is necessary to repeat the entire calculation for each  $Z$ . With the polynomial wave function, containing only a single nonlinear parameter, it was possible to obtain values for all  $Z$  with a single set of matrix elements. On the other hand, with Slater orbitals and a large number of nonlinear parameters, the configuration-interaction expansion converges to a comparable energy value with fewer terms, reducing the size of the matrix which must be handled in calculating expectation values.

Calculation of closed-form expressions for the required matrix elements is a straightforward application of methods outlined briefly in I. However, in the present work it is considerably more tedious, since for the three-electron case there are up to 18 distinct integrals in each matrix element and for the four-electron case as many as 38.

### III. RESULTS AND DISCUSSION

Form factors  $F(K)$  for both the lithium and beryllium isoelectronic sequences are given in Table I. Incoherent-scattering functions  $NS(K)$  are given in Table II. In Fig. 1 is shown a comparison of form factors obtained in the present work with values for Li I and Be I calculated by Womack and Silverman<sup>5</sup> with Hartree-Fock wave functions and by Hanson *et al.*<sup>6</sup> with Hartree-Slater wave functions. With the Hartree-Slater type of function, in which exchange is represented by an extra term in the potential rather than by use of a properly antisymmetric wave function, the additional error in energy is quite small.<sup>7</sup> However, it is clear from Fig. 1 that this approximation can lead to considerable error in the calculation of expectation values other than the total energy.

TABLE I. Atomic form factors for the Li and Be isoelectronic sequences.

$(\sin^2\theta)/\lambda$ ( $\text{\AA}^{-1}$ )	$K\alpha_0$	Li I	Be II	B III	C IV	N V	O VI	Be I	B II	C III	N IV	O V
0.0	0.0	3.0000	3.0000	3.0000	3.0000	3.0000	3.0000	4.0000	4.0000	4.0000	4.0000	4.0000
0.005	0.03324855	2.9966	2.9985	2.9993	2.9996	2.9997	2.9999	3.9970	3.9985	3.9991	3.9996	3.9997
0.006	0.03989826	2.9951	2.9980	2.9991	2.9994	2.9996	2.9999	3.9957	3.9978	3.9988	3.9993	3.9995
0.008	0.05319768	2.9914	2.9967	2.9984	2.9990	2.9993	2.9996	3.9923	3.9963	3.9978	3.9987	3.9991
0.010	0.06649710	2.9865	2.9949	2.9975	2.9984	2.9989	2.9994	3.9880	3.9943	3.9966	3.9980	3.9985
0.020	0.1329942	2.9472	2.9800	2.9938	2.9988	2.9995	2.9997	3.9525	3.9775	3.9868	3.9915	3.9939
0.030	0.1994913	2.8850	2.9573	2.9776	2.9861	2.9905	2.9933	3.8947	3.9499	3.9705	3.9806	3.9862
0.040	0.2659884	2.8044	2.9253	2.9654	2.9754	2.9832	2.9880	3.8168	3.9118	3.9479	3.9656	3.9754
0.050	0.3324855	2.7106	2.8856	2.9389	2.9618	2.9739	2.9812	3.7215	3.8640	3.9191	3.9464	3.9617
0.060	0.3989826	2.6093	2.8391	2.9130	2.9454	2.9626	2.9730	3.6118	3.8070	3.8846	3.9233	3.9451
0.080	0.5319768	2.4040	2.7300	2.8498	2.9047	2.9343	2.9522	3.3632	3.6696	3.7992	3.8654	3.9033
0.10	0.6649710	2.2190	2.6068	2.7338	2.8544	2.8990	2.9260	3.0976	3.5075	3.6948	3.7933	3.8508
0.15	0.9974565	1.9060	2.2913	2.5497	2.6967	2.7843	2.8396	2.4921	3.0496	3.3737	3.5623	3.6785
0.20	1.329942	1.7425	2.0299	2.3153	2.5129	2.6427	2.7291	2.0771	2.6067	3.0134	3.2831	3.4612
0.25	1.662427	1.6258	1.8438	2.1054	2.3259	2.4879	2.6030	1.8354	2.2463	2.6644	2.9893	3.2174
0.30	1.994913	1.5115	1.7143	1.9346	2.1527	2.3323	2.4695	1.6951	1.9840	2.3596	2.6983	2.9652
0.35	2.327398	1.3916	1.6154	1.8019	2.0022	2.1853	2.3362	1.5998	1.8044	2.1128	2.4374	2.7200
0.40	2.659884	1.2688	1.5286	1.6988	1.8765	2.0527	2.2037	1.5195	1.6822	1.9232	2.2134	2.4930
0.45	2.992369	1.1475	1.4445	1.6149	1.7734	1.9368	2.0910	1.4410	1.5945	1.7818	2.0288	2.2910
0.50	3.324855	1.0313	1.3597	1.5419	1.6885	1.8375	1.9851	1.3603	1.5246	1.6769	1.8812	2.1170
0.60	3.989826	0.82550	1.1879	1.4080	1.5530	1.6809	1.8096	1.1930	1.4020	1.5329	1.6741	1.8506
0.70	4.654797	0.65000	1.0212	1.2759	1.4392	1.5620	1.6755	1.0277	1.2793	1.4272	1.5423	1.6722
0.80	5.319768	0.51230	0.86795	1.1439	1.3309	1.4619	1.5696	0.87430	1.1526	1.3293	1.4461	1.5514
0.90	5.984739	0.40437	0.73244	1.0157	1.2231	1.3689	1.4797	0.73812	1.0268	1.2297	1.3622	1.4619
1.00	6.649710	0.32046	0.61574	0.89511	1.1162	1.2777	1.3973	0.62060	0.90669	1.1279	1.2800	1.3865
1.10	7.314681	0.25539	0.51690	0.78462	1.0121	1.1869	1.3178	0.52099	0.79575	1.0265	1.1962	1.3154
1.20	7.979652	0.20484	0.43407	0.68535	0.91283	1.0972	1.2390	0.47349	0.69558	0.92826	1.1112	1.2443
1.30	8.644623	0.16544	0.36509	0.59743	0.81998	1.0095	1.1607	0.36796	0.60659	0.83535	1.0263	1.1721
1.40	9.309594	0.13455	0.30781	0.52032	0.73439	0.92530	1.0834	0.31022	0.52841	0.74908	0.94344	1.0990
1.50	9.974565	0.11020	0.26030	0.45317	0.65640	0.84541	1.0077	0.26235	0.46026	0.67007	0.86384	1.0262
1.60	10.63954	0.09088	0.22087	0.39495	0.58596	0.77052	0.98458	0.22261	0.40114	0.59848	0.78856	0.95452
1.80	11.96948	0.06304	0.16079	0.30119	0.46632	0.63686	0.79816	0.16208	0.30590	0.47654	0.65307	0.81858
2.00	13.29942	0.04481	0.11885	0.23138	0.37154	0.52458	0.67720	0.11982	0.23500	0.37974	0.53846	0.69624
2.20	14.62936	0.03258	0.08920	0.17933	0.29708	0.43184	0.57249	0.08993	0.18213	0.30364	0.44348	0.58941
2.40	15.95930	0.02416	0.06792	0.14031	0.23875	0.35600	0.48328	0.06848	0.14250	0.24400	0.36566	0.49795
2.60	17.28925	0.01825	0.05244	0.11084	0.19300	0.29429	0.40804	0.05287	0.11257	0.19724	0.30229	0.42059
2.80	18.61919	0.01402	0.04101	0.08840	0.15701	0.24417	0.34499	0.04135	0.08977	0.16045	0.25079	0.35566
3.00	19.94913	0.01092	0.03246	0.07114	0.12858	0.20344	0.29231	0.03272	0.07224	0.13138	0.20894	0.30136
3.20	21.27910	0.00863	0.02598	0.05776	0.10599	0.17027	0.24837	0.02618	0.05865	0.10829	0.17487	0.25605
3.40	22.60901	0.00690	0.02100	0.04729	0.08793	0.14319	0.21169	0.02117	0.04802	0.08984	0.14704	0.21822
3.60	23.93896	...	0.01714	0.03903	0.07342	0.12099	0.18105	0.01728	0.03962	0.07500	0.12423	0.18662
3.80	25.26890	...	0.01412	0.03245	0.06167	0.10273	0.15339	0.01422	0.03294	0.06299	0.10547	0.16015
4.00	26.59884	...	0.01172	0.02717	0.05210	0.08763	0.13385	0.01181	0.02757	0.05322	0.08996	0.13794

TABLE I. (Continued)

$(\sin \frac{1}{2} \Theta)/\lambda$ ( $\text{\AA}^{-1}$ )	$Ka_0$	Li I	Be II	B III	C IV	N V	O VI	Be I	B II	C III	N IV	O V
4.20	27.928 78	...	0.009 81	0.022 90	0.044 27	0.075 09	0.115 72	0.009 88	0.023 23	0.045 21	0.077 08	0.119 24
4.40	29.258 72	...	0.008 26	0.019 42	0.037 81	0.064 64	0.100 41	0.008 32	0.019 70	0.038 61	0.066 34	0.103 45
4.60	30.588 67	...	...	0.016 56	0.032 46	0.055 88	0.087 43	...	0.016 80	0.033 14	0.057 35	0.090 07
4.80	31.918 61	...	...	0.014 20	0.028 01	0.048 51	0.076 40	...	0.014 41	0.028 59	0.049 78	0.078 70
5.00	33.248 55	...	...	0.012 24	0.024 27	0.042 28	0.066 99	...	0.012 42	0.024 77	0.043 38	0.068 99
5.20	34.578 49	...	...	0.010 61	0.021 12	0.036 99	0.058 93	...	0.010 75	0.021 56	0.037 95	0.060 69
5.40	35.908 43	...	...	0.009 23	0.018 46	0.032 48	0.052 01	...	0.009 36	0.018 84	0.033 32	0.053 55
5.60	37.238 38	...	...	...	0.016 20	0.028 62	0.046 04	...	...	0.016 53	0.029 36	0.047 40
5.80	38.568 32	...	...	...	0.014 27	0.025 31	0.040 88	...	...	0.014 56	0.025 95	0.042 09
6.00	39.898 26	...	...	...	0.012 61	0.022 45	0.036 40	...	...	0.012 86	0.023 02	0.037 47

With the results given here, and the results for two-electron ions reported previously, it is possible to examine the effect of ionization, through all stages, on the form factors and incoherent-scattering functions for atomic lithium and beryllium. This could be of importance both in laboratory plasma physics and in astrophysical applications.

The effect of ionization on the form factors is shown in Figs. 2 and 3. The values for the hydrogenic ions Li III and Be IV were calculated from the exact nonrelativistic expression

$$F(K) = [1 + (Ka_0/2Z)^2]^{-2}, \quad (3)$$

in which the magnitude of the momentum transfer  $K$  is related to the scattering angle  $\Theta$  and incident wavelength  $\lambda$  by

$$K = 4\pi(\sin \frac{1}{2} \Theta)/\lambda. \quad (4)$$

It can be seen from Figs. 2 and 3 that, except for very small values of the momentum transfer, the  $K$ -shell electrons have the dominant effect on the form factor. The difference in form factors for lithium beyond  $Ka_0 = 1$  and for beryllium beyond  $Ka_0 = 2$  is approximately 1%, as long as both  $K$  electrons are present, and is too small to be shown clearly on figures of this scale. Once the  $K$ -shell pair has been broken up, there is a difference of approximately (but only very approximately) a factor of 2, as might be expected.

The effect of ionization on the incoherent-scattering functions is shown in Figs. 4 and 5. In this case the values for the hydrogenic ions are given by

$$S(K) = 1 - [F(K)]^2. \quad (5)$$

Once again shell effects are evident, as shown by the humps on the curves for the three- and four-electron species. However, in this case the curves are distinct out to quite large values of the momentum transfer.

Also shown in Figs. 4 and 5 are incoherent-scattering functions for the neutral atoms obtained by Cromer and Main with Hartree-Fock wave functions.<sup>8</sup> The behavior is similar to that shown in Fig. 1 for  $F(K)$ , but greatly exaggerated, demonstrating the much greater sensitivity of  $S(K)$  to electron correlation. For Li I the difference between values of  $F(K)$  calculated with the variational wave function and those calculated with a Hartree-Fock wave function is less than 0.2% for all values of  $K$  considered, while for Be I this difference is somewhat greater than 1% for small values of  $K$ . As shown in Figs. 4 and 5, the analogous difference in  $S(K)$  for Li I is approximately 2% for all values of  $K$ , but for Be I is as much as 30% for very small values of  $K$ . It is well known that Hartree-Fock wave functions give fairly reliable ex-

TABLE II. Incoherent-scattering functions for the Li and Be isoelectronic sequences.

$(\sin \frac{1}{2} \theta) / \lambda$ ( $\text{\AA}^{-1}$ )	$K\alpha_0$	Li I	Be II	B III	C IV	N V	O VI	Be I	B II	C III	N IV	O V
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
0.005	0.033 248 55	0.006 6	0.003 3	0.001 3	0.000 8	0.0	0.0	0.004 3	0.002 7	0.001 5	0.0	0.0
0.006	0.039 898 26	0.009 6	0.004 4	0.001 9	0.001 1	0.0	0.006 3	0.003 7	0.002 1	0.001 5	0.0	0.0
0.008	0.053 197 68	0.017 0	0.007 0	0.003 2	0.002 0	0.001 6	0.011 3	0.006 1	0.003 6	0.002 1	0.000 6	0.001 3
0.010	0.066 497 10	0.026 5	0.010 4	0.005 0	0.003 1	0.002 3	0.017 7	0.009 2	0.005 4	0.003 6	0.001 5	0.002 3
0.020	0.132 994 2	0.102 2	0.038 5	0.019 8	0.012 2	0.008 6	0.070 2	0.034 8	0.020 8	0.005 4	0.013 2	0.009 7
0.030	0.199 491 3	0.216 4	0.083 6	0.044 0	0.027 4	0.018 9	0.154 4	0.076 8	0.046 3	0.030 3	0.030 3	0.022 2
0.040	0.265 988 4	0.354 1	0.143 7	0.077 1	0.048 2	0.033 2	0.265 6	0.134 0	0.081 3	0.054 1	0.054 1	0.039 4
0.050	0.332 485 5	0.499 8	0.215 9	0.118 1	0.074 5	0.051 4	0.398 1	0.204 9	0.125 5	0.084 3	0.084 3	0.061 3
0.060	0.398 982 6	0.640 4	0.297 2	0.166 2	0.105 8	0.073 3	0.545 5	0.287 8	0.178 0	0.120 5	0.120 5	0.087 8
0.080	0.531 976 8	0.874 2	0.473 8	0.279 0	0.181 6	0.127 0	0.861 0	0.481 5	0.305 0	0.209 6	0.209 6	0.153 6
0.10	0.664 971 0	1.032 8	0.649 9	0.406 0	0.271 4	0.192 4	1.170 6	0.698 6	0.455 3	0.317 9	0.317 9	0.234 9
0.15	0.997 456 5	1.245 8	0.999 2	0.728 1	0.527 1	0.390 7	1.774 2	1.247 7	0.883 3	0.646 6	0.646 6	0.490 8
0.20	1.329 94 2	1.417 6	1.205 4	0.988 5	0.777 6	0.607 6	2.479 3	2.120 7	1.695 7	1.305 1	1.007 0	0.790 3
0.25	1.662 428	1.605 2	1.346 4	1.169 7	0.985 3	0.811 3	3.664 2	2.321 5	2.009 0	1.659 6	1.348 1	1.096 7
0.30	1.994 913	1.795 3	1.478 1	1.299 4	1.143 1	0.984 2	4.835 4	2.470 5	2.220 0	1.931 5	1.641 1	1.382 3
0.35	2.327 398	1.614 4	1.614 4	1.408 3	1.262 7	1.232 9	6.079 9	2.607 9	2.371 9	2.132 9	1.878 0	1.631 8
0.40	2.659 884	1.752 7	1.752 7	1.513 5	1.360 7	1.528 5	7.473 7	2.743 7	2.494 2	2.284 5	2.064 3	1.840 6
0.45	2.992 369	2.289 8	1.888 2	1.620 4	1.449 9	1.323 8	8.854 4	2.877 1	2.605 9	2.405 1	2.211 0	2.011 4
0.50	3.324 855	2.416 6	2.017 3	1.728 5	1.537 2	1.404 0	1.293 1	3.005 3	2.713 4	2.508 4	2.329 6	2.150 7
0.60	3.989 826	2.612 9	2.248 4	1.939 9	1.713 6	1.554 0	1.435 7	3.237 4	2.921 2	2.692 6	2.518 1	2.363 2
0.70	4.654 797	2.746 2	2.437 8	1.888 7	1.888 7	1.703 6	1.566 1	3.429 1	3.114 7	2.865 2	2.677 2	2.525 6
0.80	5.319 768	2.833 9	2.585 8	2.304 8	2.054 4	1.852 6	1.696 0	3.579 4	3.286 8	3.028 9	2.825 4	2.665 7
0.90	5.984 739	2.890 9	2.697 5	2.304 8	2.054 4	1.996 2	1.825 6	3.693 1	3.433 9	3.180 4	2.966 7	2.795 8
1.00	6.649 710	2.927 8	2.780 2	2.449 1	2.205 7	1.996 2	1.951 9	3.777 1	3.555 6	3.316 6	3.100 2	2.920 1
1.10	7.314 681	2.951 7	2.840 3	2.567 8	2.339 9	2.130 6	2.072 1	3.838 3	3.653 7	3.435 9	3.224 0	3.038 8
1.20	7.979 652	2.967 4	2.883 8	2.738 9	2.455 3	2.253 5	2.072 1	3.882 5	3.731 5	3.538 1	3.336 5	3.150 9
1.30	8.644 623	2.977 7	2.915 1	2.797 9	2.555 4	2.363 8	2.184 3	3.914 4	3.792 3	3.624 0	3.436 8	3.255 2
1.40	9.309 594	2.984 5	2.937 7	2.843 7	2.638 4	2.461 4	2.287 5	3.914 4	3.839 5	3.695 3	3.524 8	3.350 9
1.50	9.974 565	2.989 2	2.954 0	2.879 0	2.763 3	2.546 4	2.381 0	3.937 3	3.895 8	3.753 7	3.601 1	3.437 4
1.60	10.639 54	2.992 3	2.965 8	2.906 1	2.808 9	2.619 6	2.464 9	3.953 8	3.875 9	3.801 3	3.666 3	3.514 7
1.80	11.969 48	2.996 0	2.980 7	2.943 0	2.875 6	2.682 1	2.539 4	3.965 8	3.903 8	3.801 3	3.666 3	3.514 7
2.00	13.299 42	2.997 8	2.988 8	2.964 8	2.918 6	2.779 3	2.661 9	3.980 9	3.941 8	3.870 7	3.768 2	3.642 9
2.20	14.629 36	2.998 8	2.993 3	2.977 9	2.946 3	2.847 3	2.754 0	3.989 0	3.964 3	3.915 6	3.839 7	3.739 9
2.40	15.959 30	2.999 23	2.995 9	2.985 9	2.964 2	2.894 3	2.821 8	3.993 5	3.977 7	3.944 4	3.889 1	3.811 5
2.60	17.289 25	2.999 58	2.997 4	2.990 8	2.975 8	2.926 5	2.871 0	3.996 1	3.985 8	3.963 1	3.923 0	3.863 6
2.80	18.619 19	2.999 74	2.998 3	2.993 9	2.983 5	2.963 7	2.906 4	3.997 6	3.990 8	3.975 2	3.946 2	3.901 2
3.00	19.949 13	3.999 84	2.998 9	2.995 9	2.988 5	2.974 2	2.950 2	3.999 02	3.994 0	3.983 1	3.962 2	3.928 2
3.20	21.279 07	2.999 90	2.999 28	2.997 2	2.992 0	2.981 4	2.963 3	3.999 36	3.996 0	3.988 4	3.973 2	3.947 5
3.40	22.609 01	2.999 93	2.999 56	2.998 0	2.994 3	2.986 5	2.972 8	3.999 57	3.997 3	3.991 9	3.980 8	3.961 5
3.60	23.938 96	...	2.999 71	2.998 6	2.995 9	2.990 1	2.979 7	3.999 71	3.998 1	3.994 3	3.986 1	3.971 5
3.80	25.268 90	...	2.999 80	2.999 0	2.997 0	2.992 7	2.984 8	...	3.999 08	3.995 9	3.989 9	3.978 8
4.00	26.598 84	...	2.999 86	2.999 28	2.997 8	2.994 6	2.988 5	...	3.999 34	3.997 8	3.994 5	3.988 0

TABLE II. (Continued)

$(\sin^2\theta)/\lambda$ ( $\text{\AA}^{-1}$ )	$K\alpha_0$	Li I	Be II	B III	C IV	N V	O VI	Be I	B II	C III'	N IV	O V
4.20	27.92878	...	...	2.99947	2.9984	2.9959	2.9912	...	3.99952	3.9984	3.9959	3.9909
4.40	29.25872	...	...	2.99961	2.9988	2.9969	2.9932	...	...	3.9988	3.9969	3.9930
4.60	30.58867	...	...	2.99971	2.99907	2.9976	2.9948	...	...	3.99912	3.9976	3.9946
4.80	31.91861	...	...	...	2.99929	2.9982	2.9959	...	...	3.99934	3.9982	3.9958
5.00	33.24855	...	...	...	2.99946	2.9986	2.9968	...	...	...	3.9986	3.9968
5.20	34.57849	...	...	...	2.99957	2.9989	2.9974	...	...	...	3.9989	3.9975
5.40	35.90843	...	...	...	...	2.99912	2.9980	...	...	...	3.99916	3.9980
5.60	37.23838	...	...	...	...	2.99931	2.9984	...	...	...	...	3.9984
5.80	38.56832	...	...	...	...	2.99945	2.9987	...	...	...	...	3.9987
6.00	39.89826	...	...	...	...	2.99956	3.9990	...	...	...	...	3.9990

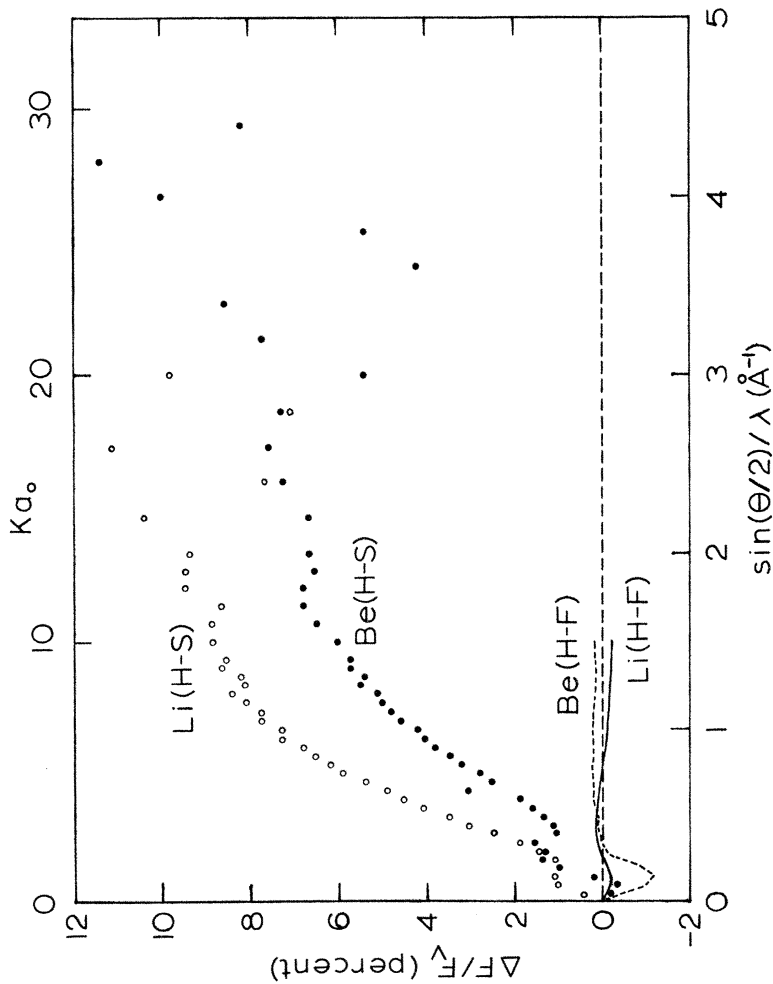


FIG. 1. Comparison of form factor calculations for lithium and beryllium.  $\Delta F$  is the difference between the Hartree-Fock (HF) or Hartree-Slater (HS) value and the value  $F_V$  obtained with a variational wave function.

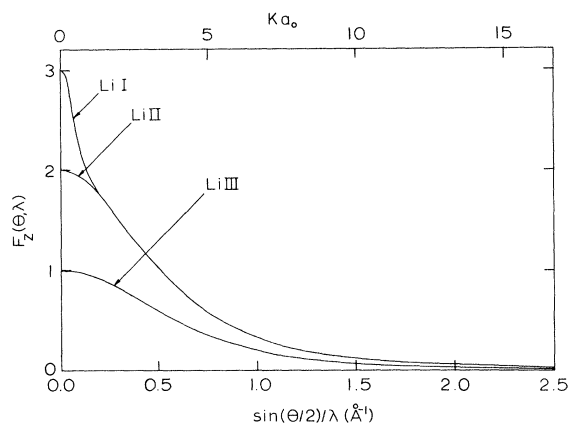


FIG. 2. Effect of ionization on the atomic form factor for lithium.

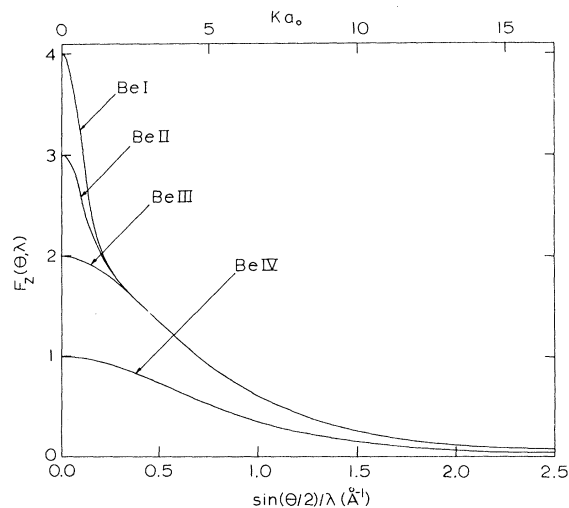


FIG. 3. Effect of ionization on the atomic form factor for beryllium.

pectation values of one-electron operators, such as appear in  $F(K)$ . However, this is not true for two-electron operators,<sup>2,9</sup> which are much more sensitive to the accuracy of the wave function.

#### ACKNOWLEDGMENT

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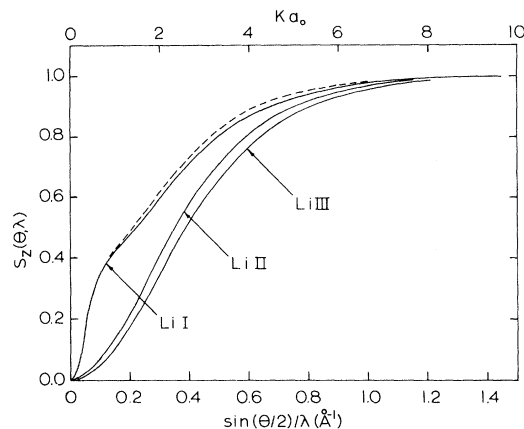


FIG. 4. Effect of ionization on the incoherent-scattering function for lithium. Dashed curve represents the Hartree-Fock value for the neutral atom.

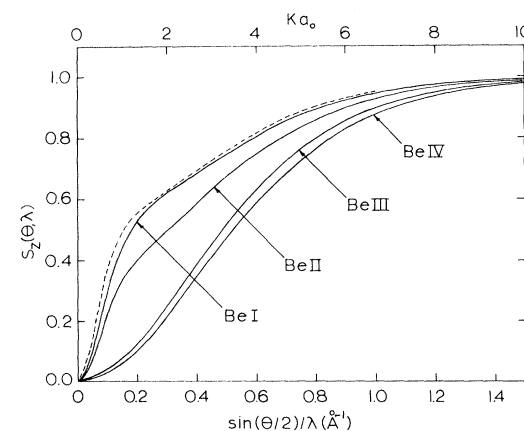


FIG. 5. Effect of ionization on the incoherent-scattering function for beryllium. Dashed curve represents the Hartree-Fock value for the neutral atom.

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PHYSICAL REVIEW A

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## Studies of the Statistical Exchange Approximation in First-Transition-Row Atoms and Ions: $Mn^{+2}$ Ion†

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A study of several statistical approximations to the Hartree-Fock (HF) one-electron effective exchange potential has been carried out through a series of restricted and spin-polarized Hartree-Fock-Slater (HFS) calculations on 3d-transition-row atoms and ions. The results of this study for the  $Mn^{+2}$  ion are reported in this paper and are compared with the corresponding HF results. Of the various approximations in which only the homogeneous part of the local exchange potential is kept, the simple  $X\alpha$  method is shown to give quite good results. This method amounts to multiplying the exchange potential  $-6[(3/4\pi)\rho_\xi(r)]^{1/3}$ , where  $\xi = \pm\frac{1}{2}$ , by a constant  $\alpha$  which is usually determined by the requirement that the  $X\alpha$  orbitals correspond to a minimum in the HF energy. It is shown that the energy-dependent exchange schemes proposed earlier break down totally in the spin-polarized case. We examine the importance of including the inhomogeneous correction terms via the method recently proposed by Herman *et al.* and we discuss the possible importance of these terms in spin-polarized energy-band calculations. We conclude that the  $X\alpha$  method is both accurate and simple enough for practical use in carrying out energy-band calculations for magnetic solids.

### I. INTRODUCTION

Over the last few years, substantial improvements have been made in the methods used in calculating the electronic structure of atoms, molecules, and solids. This is in part due to the development of larger and faster digital computers, which has made possible the large configuration interaction and projected Hartree-Fock (HF) calculations on many of the atoms and ions in the first two rows of the periodic table. To some extent, these advances have been carried over into the calculation of the electronic structure of small diatomic molecules. For the transition-row and larger atoms, such calculations have not yet been made, but there do exist accurate restricted<sup>1</sup> and spin-polarized Hartree-Fock<sup>2</sup> (RHF and SPHF) calculations. One of the important results of these calculations is that they have enabled investigators to accurately assess the ability of the one-electron picture to describe the electronic structure of atoms and molecules.

However, despite these advances, a "true" HF calculation for a solid remains to be done. This is largely due to the problems that arise by introducing the nonlocal HF exchange potential into the one-electron differential equation and in evaluating

the multicenter integrals. For these reasons, the majority of the studies of the electronic structure of solids have been made using one form or another of the free-electron exchange approximation suggested by one of us (JCS) earlier.<sup>3</sup>

One of the many interesting results which has come out of these studies<sup>4,5</sup> is that several investigators have found that if they used the form of this exchange approximation as originally proposed by Slater, their results were in somewhat poorer agreement with the de Haas-Van Alphen experiments, the optical densities of states, and the magnetic properties of these solids than if they used the form suggested by Kohn and Sham<sup>6</sup> and by Gaspar,<sup>7</sup> which differs from that of Slater by a factor of  $\frac{2}{3}$ . Furthermore, they conclude that a factor somewhere between 1.0 and  $\frac{2}{3}$  would lead to even better agreement with the experimental findings. This is especially true of the recent spin-polarized energy-band investigations of the electronic structure of the first-row transition metals<sup>4</sup> and of transition-metal compounds in their magnetically aligned states.<sup>8</sup> This theory relaxes the constraint (imposed in the conventional energy-band theory) that the spatial orbitals associated with each one-electron state be doubly occupied by one  $\uparrow$  and one  $\downarrow$  spin electron.<sup>9</sup> This leads to two sets of