

The density matrix formalism developed here provides a general extension of the usual Waller–Hartree equations and therefore facilitates a study of the importance of effects other than electron exchange; that is, we are in a favorable position to assess the importance of electron correlation on X-ray scattering. This topic is treated in the next paper where we compare coherent and total intensity values obtained for the Be atom from the NSO and NSG analysis of a configuration interaction (CI) function, and from a two-configuration function, with those computed within the Waller–Hartree formalism from a HF function.

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## Correlation and X-ray Scattering. II. Atomic Beryllium

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In order to assess the importance of correlation effects with respect to the Hartree–Fock (HF) results, values of the coherent, total and incoherent scattered X-ray intensities were computed for the  $1S$  ground state of atomic beryllium. Natural spin orbitals (NSO) and natural spin geminals (NSG) constructed from the accurate configuration interaction (CI) wavefunction of A. W. Weiss were used in the evaluation of these X-ray quantities from previously derived density matrix expressions. Values were also computed from the two-configuration wavefunction of Watson, which accounts for the  $2s-2p$  near degeneracy effect. As expected, the CI results for the total intensity differ from their HF counterparts but the magnitudes of the absolute deviations are not as large as those observed for the coherent intensity values. Although the HF results for the coherent intensity are in reasonably good agreement with the CI values, conclusions based on the Møller–Plesset theorem must be made with caution. The largest percentage deviations between HF and CI results, however, are observed for the incoherent intensity. All calculations reported here were verified by the use of sum rules.

### 1. Introduction

In this paper we examine the effects of electron correlation on the coherent, incoherent and total intensities (the sum of the Compton and Rayleigh contributions) of scattered X-ray radiation. Total intensity values computed from Hartree–Fock (HF) wavefunctions are expected to be somewhat erroneous since an independent particle model (IPM) description of the atom assumes that the spatial coordinates of each electron are in fact independent of the spatial coordinates of

the remaining electrons. This neglect of the so-called ‘Coulomb holes’ associated with electron pairs can lead to errors when evaluating the total intensity expression since the scattering operator contains the inter-electron distances  $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ . These coulombic manifestations of correlation must not be confused with exchange effects since exchange terms, which do enter the IPM (Waller–Hartree, 1929) expression for the total scattered intensity, owe their existence only to the antisymmetric behaviour of the HF wavefunction. Thus antisymmetry leads to an exchange corre-

lation between electrons of like spin – the so-called ‘Fermi hole’ discussed by Löwdin (1959).

With respect to the accuracy of coherent X-ray scattering factors computed from HF wavefunctions, reference can be made to the Møller–Plesset (1934) theorem\* which states that these quantities must be accurate to second order (in the sense of a perturbation treatment) since they are expectation values of an one-electron operator. However, the coherent scattering factor  $F(\mu)$  is related to the Fourier transform of the charge density matrix  $\bar{\gamma}(\mathbf{r})$  and this function may not be represented equally well in all regions of space within the HF approximation. This means, of course, that the accuracy of HF form factors is a function of the scattering variable.

In the next section we use a density matrix formalism derived in the preceding paper (Benesch & Smith (1970), hereafter referred to as I) to obtain ‘accurate’ correlated values of the coherent, incoherent and total scattered X-ray intensities for the  $1S$  ground state of atomic Be. The natural spin orbitals (NSO) and natural spin geminals (NSG) used in the present calculations are those obtained by Barnett & Shull (1967)

\* See Nesbet (1965) for the extension of this theorem to non-closed shell systems.

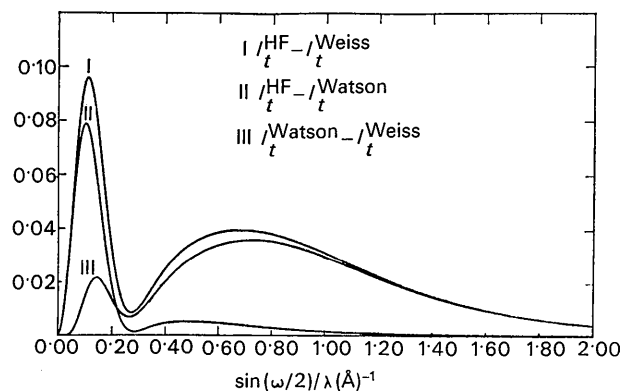


Fig. 1. Intensity differences for total scattering for the  $1S$  state of the Be atom.

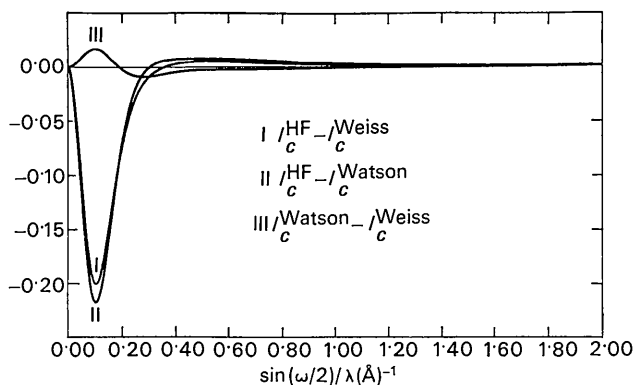


Fig. 2. Intensity differences for coherent scattering for the  $1S$  state of the Be atom.

from the accurate (93.06% of the correlation energy, 55 configurations) configuration interaction (CI) function of A. Weiss W. (Weiss, 1961). Values were also obtained from Watson's (1961) two-configuration wavefunction (46.07% of the correlation energy) and from Clementi's (1965) analytical HF function (0% of the correlation energy).

## 2. Results

Values of the coherent  $I_c$ , incoherent  $I_i$  and total  $I_t$  intensities of scattered X-ray radiation computed from the three wavefunctions mentioned above are presented in Table 1 at various intervals of  $\sin(\omega/2)/\lambda$ , in  $\text{\AA}^{-1}$ . For a  $1S$  state the scattering variable  $\mu = 2\pi|\mathbf{S}|$  depends only on the magnitude of the scattering vector  $\mathbf{S}$  and not on its direction. For purposes of illustration the various differences in total intensity  $\Delta I_t(\mu)$  are plotted versus  $\sin(\omega/2)/\lambda$  in Fig. 1. Fig. 2 displays the coherent intensity differences  $\Delta I_c(\mu)$ . To zero order in the incident X-ray energy, the correlated values for  $I_i(\mu)$  were obtained by subtracting the coherent from the total intensity values.

A few remarks regarding the present computations are in order. The HF results (Benesch, 1967; Tavard, Nicholas & Roualt, 1967) were obtained by evaluating the Waller–Hartree (1929) expressions for  $I_c(\mu)$  and  $I_i(\mu)$ . Watson's (1961) two-configuration function, which takes into account the effects of the near degeneracy of  $2s$  and  $2p$  orbitals (Linderberg & Shull, 1960; Layzer, 1959) is written as

$$\Psi_g = a\Psi_1 + b\Psi_2, \quad (1)$$

where  $a$  and  $b$  are optimized mixing parameters and  $a^2 + b^2 = 1$ . The functions  $\Psi_1$ ,  $\Psi_2$  have the definitions

$$\Psi_1 = [1s\alpha(1) 1s\beta(2) 2s\alpha(3) 2s\beta(4)], \quad (2a)$$

$$\Psi_2 = \frac{1}{\sqrt{3}} \left\{ [1s\alpha(1) 1s\beta(2) 2p_+\alpha(3) 2p_-\beta(4)] \right. \\ \left. + [1s\alpha(1) 1s\beta(2) 2p_-\alpha(3) 2p_+\beta(4)] \right. \\ \left. - [1s\alpha(1) 1s\beta(2) 2p_0\alpha(3) 2p_0\beta(4)] \right\} \quad (2b)$$

where the bracket notation  $[ ]$  indicates a normalized Slater determinant constructed from the orthonormal atomic orbitals  $1s, 2s$ , and  $2p_+, 2p_-, 2p_0$ . The atomic orbitals are expanded in a Slater-type orbital (STO) basis  $\{\varphi_j(\mathbf{r})\}$ ; the  $+$ ,  $-$ ,  $0$  subscripts refer to the  $z$  component ( $m_l$  quantum number) of angular momentum for the threefold degenerate  $2p$  orbitals. With Watson's  $1S$  state wavefunction the expressions for the coherent and total scattered X-ray intensities are easily shown to be

$$I_c/I_{c1} = |2f_{1s1s} + 2a^2f_{2s2s} + 2b^2f_{2p(0)2p}|^2, \quad (3a)$$

$$I_t/I_{c1} = 2a^2[f_{1s1s}^2 + 4f_{1s1s}f_{2s2s} + f_{2s2s}^2 - 2f_{1s2s}^2] \\ - 4ab\sqrt{3}f_{2s(1)2p}^2 \\ + 2b^2[f_{1s1s}^2 + 4f_{1s1s}f_{2p(0)2p} + f_{2p(0)2p}^2 + 2f_{2p(2)2p}^2 \\ - 2f_{1s(1)2p}^2] + 4. \quad (3b)$$

The matrix elements appearing in (3a) and (3b) are similar to those defined by equation (24e) of I. The subscripts  $s, p$  define the values of the angular momentum quantum numbers  $l_1, l_2$  of the two atomic orbitals

involved in the particular matrix element while the bracketed subscript refers to the order  $p$  of the spherical Bessel function,  $|l_1 - l_2| \leq p \leq l_1 + l_2$ . Since each atomic orbital is expanded over a STO basis  $\{\phi_i(\mathbf{r})\}$ ,

Table 1. Total coherent and incoherent scattered X-ray intensities for the Be atom in the ground state ( $1S$ ).

$K^*$	$I_a^a(\mu)$	$I_b^b(\mu)$	$I_c^c(\mu)$	$I_a^a(\mu)$	$I_b^b(\mu)$	$I_c^c(\mu)$	$I_a^a(\mu)$	$I_b^b(\mu)$	$I_c^c(\mu)$
0-000	16-0004	16-00000	15-99972	16-0005	16-00000	16-00001	-0-0001	0-00000	-0-00028
0-005	15-9813	15-98043	15-98017	15-9750	15-97606	15-97597	0-0062	0-00437	0-00420
0-010	15-9242	15-92199	15-92178	15-8989	15-90459	15-90420	0-0252	0-01740	0-01758
0-015	15-8298	15-82550	15-82535	15-7733	15-78656	15-78568	0-0565	0-03893	0-03967
0-020	15-6996	15-69226	15-69218	15-6002	15-62360	15-62204	0-0994	0-06866	0-07014
0-025	15-5351	15-52408	15-52403	15-3819	15-41789	15-41549	0-1532	0-10619	0-10855
0-030	15-3385	15-32319	15-32312	15-1217	15-17216	15-16877	0-2168	0-15103	0-15435
0-035	15-1124	15-09217	15-09200	14-8232	14-88956	14-88506	0-2892	0-20261	0-20694
0-040	14-8595	14-83393	14-83355	14-4904	14-57366	14-56795	0-3691	0-26027	0-26559
0-045	14-5828	14-55160	14-55087	14-1277	14-22826	14-22129	0-4551	0-32334	0-32958
0-050	14-2855	14-24847	14-24723	13-7395	13-85740	13-84912	0-5460	0-39107	0-39811
0-055	13-9708	13-92793	13-92601	13-3304	13-46520	13-45561	0-6404	0-46272	0-47040
0-060	13-6420	13-59335	13-59058	12-9050	13-05581	13-04494	0-7370	0-53754	0-54564
0-065	13-3023	13-24810	13-24430	12-4678	12-63332	12-62123	0-8345	0-61478	0-62307
0-070	12-9548	12-89540	12-89041	12-0229	12-20168	12-18847	0-9318	0-69372	0-70194
0-075	12-6024	12-53833	12-53201	11-5745	11-76467	11-75045	1-0279	0-77366	0-78157
0-080	12-2480	12-17977	12-17200	11-1262	11-32580	11-31071	1-1219	0-85397	0-86130
0-085	11-8942	11-82236	11-81306	10-6813	10-88832	10-87251	1-2129	0-93404	0-94055
0-090	11-5431	11-46848	11-45761	10-2428	10-45515	10-43880	1-3004	1-01333	1-01881
0-095	11-1970	11-12026	11-10780	9-8132	10-02889	10-01218	1-3838	1-09137	1-09562
0-100	10-8576	10-77952	10-76551	9-3948	9-61180	9-59492	1-4628	1-16772	1-17059
0-105	10-5264	10-44783	10-43234	8-9893	9-20581	9-18894	1-5371	1-24202	1-24340
0-110	10-2049	10-12648	10-10961	8-5982	8-81250	8-79583	1-6066	1-31399	1-31379
0-115	9-8940	9-81651	9-79841	8-2227	8-43315	8-41685	1-6713	1-38336	1-38155
0-120	9-5946	9-51872	9-49954	7-8634	8-06875	8-05299	1-7312	1-44997	1-44655
0-125	9-3074	9-23368	9-21361	7-5209	7-72001	7-70493	1-7865	1-51368	1-50868
0-130	9-0328	8-96177	8-94101	7-1956	7-38738	7-37312	1-8372	1-57439	1-56789
0-135	8-7711	8-70319	8-68195	6-8873	7-07112	7-05780	1-8838	1-63208	1-62415
0-140	8-5224	8-45800	8-43648	6-5961	6-77127	6-75898	1-9263	1-68673	1-67750
0-145	8-2867	8-22610	8-20451	6-3216	6-48771	6-47654	1-9651	1-73838	1-72797
0-150	8-0639	8-00730	7-98584	6-0635	6-22020	6-21019	2-0004	1-78710	1-77564
0-155	7-8538	7-80131	7-78015	5-8211	5-96835	5-95956	2-0327	1-83296	1-82060
0-160	7-6560	7-60777	7-58709	5-5939	5-73169	5-72414	2-0621	1-87607	1-86295
0-165	7-4704	7-42626	7-40619	5-3813	5-50969	5-50339	2-0890	1-91657	1-90280
0-170	7-2963	7-25631	7-23699	5-1826	5-30175	5-29670	2-1137	1-95457	1-94029
0-175	7-1335	7-09745	7-07896	4-9971	5-10723	5-10341	2-1364	1-99022	1-97555
0-180	6-9813	6-94914	6-93157	4-8240	4-92546	4-92285	2-1573	2-02368	2-00872
0-185	6-8395	6-81087	6-79426	4-6627	4-75578	4-75433	2-1767	2-05509	2-03993
0-190	6-7073	6-68211	6-66649	4-5124	4-59750	4-59717	2-1949	2-08461	2-06932
0-195	6-5843	6-56233	6-54771	4-3724	4-44995	4-45069	2-2119	2-11238	2-09702
0-200	6-4701	6-45102	6-43738	4-2421	4-31247	4-31421	2-2281	2-13855	2-12317
0-205	6-3641	6-34766	6-33499	4-1207	4-18440	4-18708	2-2434	2-16326	2-14790
0-210	6-2658	6-25178	6-24001	4-0077	4-06512	4-06868	2-2581	2-18666	2-17133
0-215	6-1748	6-16288	6-15198	3-9025	3-95403	3-95840	2-2723	2-20886	2-19358
0-220	6-0906	6-08052	6-07041	3-8045	3-85054	3-85565	2-2861	2-22998	2-21476
0-225	6-0126	6-00427	5-99487	3-7131	3-75412	3-75990	2-2995	2-25015	2-23497
0-230	5-9406	5-93369	5-92492	3-6279	3-66423	3-67061	2-3128	2-26946	2-25431
0-235	5-8741	5-86841	5-86018	3-5483	3-58039	3-58730	2-3258	2-28802	2-27288
0-240	5-8127	5-80804	5-80027	3-4740	3-50212	3-50950	2-3387	2-30591	2-29076
0-245	5-7560	5-75222	5-74482	3-4045	3-42900	3-43679	2-3515	2-32321	2-30803
0-250	5-7037	5-70062	5-69350	3-3395	3-36061	3-36874	2-3643	2-34001	2-32476
0-255	5-6555	5-65293	5-64599	3-2784	3-29657	3-30498	2-3770	2-35635	2-34101
0-260	5-6110	5-60884	5-60201	3-2211	3-23653	3-24515	2-3898	2-37231	2-35685
0-265	5-5699	5-56808	5-56127	3-1672	3-18013	3-18893	2-4026	2-38794	2-37234
0-270	5-5320	5-53038	5-52352	3-1164	3-12709	3-13601	2-4155	2-40329	2-38751
0-275	5-4969	5-49549	5-48851	3-0685	3-07710	3-08610	2-4284	2-41839	2-40241
0-280	5-4646	5-46319	5-45602	3-0231	3-02990	3-03894	2-4414	2-43329	2-41708
0-285	5-4346	5-43327	5-42584	2-9801	2-98525	2-99428	2-4545	2-44802	2-43156
0-290	5-4069	5-40551	5-39777	2-9393	2-94290	2-95190	2-4676	2-46261	2-44587
0-295	5-3812	5-37973	5-37163	2-9004	2-90266	2-91158	2-4809	2-47707	2-46004
0-300	5-3574	5-35577	5-34725	2-8632	2-86433	2-87315	2-4942	2-49144	2-47410
0-310	5-3145	5-31262	5-30317	2-7936	2-79267	2-80121	2-5210	2-51995	2-50195
0-320	5-2772	5-27490	5-26439	2-7292	2-72665	2-73485	2-5480	2-54825	2-52955

Table 1 (cont.)

$K^*$	$I_i^a(\mu)$	$I_i^b(\mu)$	$I_i^c(\mu)$	$I_c^a(\mu)$	$I_c^b(\mu)$	$I_c^c(\mu)$	$I_i^a(\mu)$	$I_i^b(\mu)$	$I_i^c(\mu)$
0-330	5-2443	5-24162	5-22997	2-6690	2-66521	2-67299	2-5753	2-57641	2-55697
0-340	5-2150	5-21192	5-19907	2-6122	2-60743	2-61478	2-6028	2-60449	2-58429
0-350	5-1885	5-18510	5-17100	2-5581	2-55258	2-55946	2-6304	2-63251	2-61154
0-360	5-1643	5-16053	5-14518	2-5061	2-50004	2-50645	2-6581	2-66049	2-63873
0-370	5-1418	5-13772	5-12113	2-4558	2-44930	2-45525	2-6859	2-68842	2-66588
0-380	5-1205	5-11624	5-09844	2-4068	2-39995	2-40545	2-7137	2-71630	2-69298
0-390	5-1003	5-09576	5-07676	2-3588	2-35166	2-35674	2-7415	2-74411	2-72002
0-400	5-0807	5-07600	5-05585	2-3115	2-30417	2-30886	2-7692	2-77183	2-74699
0-410	5-0616	5-05673	5-03547	2-2648	2-25728	2-26161	2-7968	2-79945	2-77385
0-420	5-0428	5-03777	5-01545	2-2184	2-21084	2-21485	2-8243	2-82693	2-80060
0-430	5-0241	5-01900	4-99566	2-1724	2-16474	2-16846	2-8517	2-85426	2-82721
0-440	5-0055	5-00031	4-97601	2-1266	2-11889	2-12236	2-8789	2-88141	2-85365
0-450	4-9868	4-98162	4-95641	2-0810	2-07326	2-07650	2-9058	2-90836	2-87991
0-460	4-9681	4-96289	4-93682	2-0356	2-02781	2-03085	2-9326	2-93509	2-90596
0-470	4-9494	4-94409	4-91720	1-9903	1-98253	1-98541	2-9590	2-96156	2-93179
0-480	4-9305	4-92519	4-89753	1-9452	1-93742	1-94017	2-9852	2-98777	2-95736
0-490	4-9115	4-90620	4-87781	1-9003	1-89252	1-89515	3-0112	3-01368	2-98266
0-500	4-8924	4-88712	4-85805	1-8556	1-84783	1-85038	3-0367	3-03929	3-00767
0-510	4-8732	4-86796	4-83825	1-8112	1-80339	1-80587	3-0620	3-06456	3-03238
0-520	4-8539	4-84874	4-81843	1-7670	1-75924	1-76166	3-0869	3-08950	3-05677
0-530	4-8346	4-82949	4-79862	1-7231	1-71542	1-71779	3-1115	3-11407	3-08083
0-540	4-8153	4-81023	4-77883	1-6796	1-67195	1-67430	3-1357	3-13827	3-10454
0-550	4-7960	4-79099	4-75910	1-6365	1-62890	1-63121	3-1595	3-16209	3-12788
0-560	4-7767	4-77179	4-73944	1-5938	1-58629	1-58858	3-1829	3-18550	3-15086
0-570	4-7575	4-75267	4-71990	1-5516	1-54416	1-54644	3-2059	3-20851	3-17345
0-580	4-7384	4-73365	4-70048	1-5100	1-50255	1-50482	3-2285	3-23110	3-19566
0-590	4-7195	4-71476	4-68123	1-4688	1-46149	1-46376	3-2506	3-25327	3-21747
0-600	4-7007	4-69603	4-66216	1-4283	1-42103	1-42329	3-2724	3-27500	3-23887
0-620	4-6636	4-65913	4-62467	1-3491	1-34198	1-34423	3-3145	3-31715	3-28045
0-640	4-6274	4-62312	4-58819	1-2725	1-26560	1-26783	3-3549	3-35752	3-32036
0-660	4-5922	4-58816	4-55286	1-1987	1-19207	1-19427	3-3935	3-39609	3-35858
0-680	4-5583	4-55436	4-51879	1-1279	1-12151	1-12367	3-4303	3-43286	3-39512
0-700	4-5255	4-52182	4-48608	1-0602	1-05399	1-05610	3-4654	3-46783	3-42997
0-720	4-4941	4-49060	4-45478	0-9955	0-98956	0-99162	3-4986	3-50105	3-46316
0-740	4-4641	4-46076	4-42495	0-9339	0-92823	0-93023	3-5302	3-53252	3-49472
0-760	4-4354	4-43230	4-39659	0-8754	0-87000	0-87192	3-5600	3-56230	3-52467
0-780	4-4082	4-40524	4-36972	0-8199	0-81481	0-81666	3-5883	3-59043	3-55307
0-800	4-3824	4-37958	4-34432	0-7675	0-76262	0-76438	3-6149	3-61696	3-57994
0-820	4-3579	4-35529	4-32037	0-7179	0-71334	0-71502	3-6400	3-64195	3-60536
0-840	4-3348	4-33235	4-29784	0-6712	0-66688	0-66848	3-6636	3-66547	3-62936
0-860	4-3130	4-31071	4-27667	0-6272	0-62316	0-62467	3-6858	3-68756	3-65201
0-880	4-2925	4-29034	4-25683	0-5859	0-58205	0-58348	3-7066	3-70829	3-67335
0-900	4-2732	4-27119	4-23827	0-5471	0-54346	0-54481	3-7261	3-72774	3-69346
0-920	4-2551	4-25321	4-22091	0-5106	0-50726	0-50853	3-7444	3-74596	3-71238
0-940	4-2381	4-23635	4-20472	0-4765	0-47334	0-47454	3-7616	3-76301	3-73018
0-960	4-2222	4-22055	4-18962	0-4446	0-44159	0-44272	3-7776	3-77896	3-74690
0-980	4-2073	4-20575	4-17557	0-4147	0-41189	0-41295	3-7926	3-79387	3-76261
1-000	4-1933	4-19192	4-16250	0-3867	0-38412	0-38513	3-8066	3-80780	3-77737
1-100	4-1363	4-13531	4-10991	0-2725	0-27067	0-27142	3-8638	3-86465	3-83849
1-200	4-0961	4-09542	4-07407	0-1921	0-19082	0-19139	3-9040	3-90460	3-88267
1-300	4-0680	4-06748	4-04988	0-1358	0-13493	0-13539	3-9321	3-93255	3-91449
1-400	4-0483	4-04795	4-03364	0-0965	0-09588	0-09624	3-9518	3-95207	3-93741
1-500	4-0345	4-03428	4-02276	0-0690	0-06854	0-06882	3-9655	3-96574	3-95394
1-600	4-0248	4-02467	4-01545	0-0497	0-04933	0-04956	3-9752	3-97534	3-96590
1-700	4-0180	4-01788	4-01054	0-0360	0-03576	0-03594	3-9820	3-98212	3-97459
1-800	4-0132	4-01306	4-00722	0-0263	0-02612	0-02627	3-9869	3-98694	3-98095
1-900	4-0097	4-00962	4-00496	0-0194	0-01923	0-01934	3-9903	3-99039	3-98562
2-000	4-0072	4-00713	4-00342	0-0144	0-01427	0-01436	3-9928	3-99287	3-98907
2-100	4-0054	4-00533	4-00237	0-0107	0-01066	0-01073	3-9946	3-99467	3-99164
2-200	4-0040	4-00402	4-00165	0-0081	0-00803	0-00809	3-9960	3-99599	3-99356
2-300	4-0031	4-00305	4-00115	0-0061	0-00609	0-00614	3-9969	3-99695	3-99501
2-400	4-0023	4-00233	4-00080	0-0047	0-00466	0-00469	3-9977	3-99767	3-99611
2-500	4-0018	4-00179	4-00056	0-0036	0-00358	0-00361	3-9982	3-99821	3-99695
2-600	4-0014	4-00139	4-00039	0-0028	0-00277	0-00280	3-9986	3-99861	3-99760
2-700	4-0011	4-00108	4-00028	0-0022	0-00216	0-00218	3-9989	3-99892	3-99810
2-800	4-0009	4-00085	4-00019	0-0017	0-00170	0-00171	3-9991	3-99915	3-99848
2-900	4-0007	4-00067	4-00014	0-0013	0-00134	0-00135	3-9993	3-99933	3-99879
3-000	4-0005	4-00053	4-00010	0-0011	0-00106	0-00107	3-9995	3-99947	3-99902
3-100	4-0004	4-00042	4-00007	0-0009	0-00085	0-00085	3-9996	3-99958	3-99921
3-200	4-0003	4-00034	4-00005	0-0007	0-00068	0-00069	3-9997	3-99966	3-99936

Table 1 (cont.)

$K^*$	$I_t^a(\mu)$	$I_t^b(\mu)$	$I_t^c(\mu)$	$I_c^a(\mu)$	$I_c^b(\mu)$	$I_c^c(\mu)$	$I_t^a(\mu)$	$I_t^b(\mu)$	$I_t^c(\mu)$
3-300	4-0003	4-00027	4-00003	0-0006	0-00055	0-00055	3-9997	3-99973	3-99948
3-400	4-0002	4-00022	4-00002	0-0004	0-00044	0-00045	3-9998	3-99978	3-99957
3-500	4-0002	4-00018	4-00002	0-0004	0-00036	0-00036	3-9998	3-99982	3-99965
3-600	4-0001	4-00015	4-00001	0-0003	0-00030	0-00030	3-9999	3-99985	3-99971
3-700	4-0001	4-00012	4-00001	0-0002	0-00024	0-00025	3-9999	3-99988	3-99976
3-800	4-0001	4-00010	4-00001	0-0002	0-00020	0-00020	3-9999	3-99990	3-99980
3-900	4-0001	4-00008	4-00000	0-0002	0-00017	0-00017	3-9999	3-99992	3-99984
4-000	4-0001	4-00007	4-00000	0-0001	0-00014	0-00014	3-9999	3-99993	3-99986

\*  $K = \sin(\omega/2)/\lambda$  ( $\text{\AA}^{-1}$ );  $\mu = 4\pi K$ .

(a) Calculated from the analytical HF wavefunction of Clementi (1965).

(b) Calculated from the analytical two-configuration wavefunction of Watson (1961).

(c) Calculated from the 55 term CI wavefunction of A. W. Weiss (Weiss, 1961) via the NSO and NSG analysis of Barnett (1965).

each  $f_{ij}$  appearing in (3a) and (3b) involves a double summation over the STO basis rather than single STO's  $\varphi_i$ ,  $\varphi_j$  as is the case with the definition (24e) of I.

Barnett, Linderberg & Shull's (1965) 1-matrix analysis of Weiss's (1961) CI Be wavefunction involves 17 NSO's of  $s$ -,  $p$ -,  $d$ - and  $f$ -type symmetry. Each NSO in turn is expanded over a STO basis of the proper symmetry. The sum of the 1-matrix eigenvalues is 4-0 to six-figure accuracy and we therefore find that  $I_c(0)/I_{c1} = 16$ , a result in agreement with the general observations of § 2B of I. A straightforward evaluation of (14-I) yields the CI values for  $I_c(\mu)/I_{c1}$  when  $\omega \neq 0$ .

Relative to the 1-matrix, the Weiss 2-matrix is rather complex since it contains a total of 185 non-zero eigenvalues. However, only the first 50 NSG (ordered in decreasing magnitude of their occupation numbers) have eigenvalues greater than  $1 \times 10^{-5}$  and the sum of these is 5-99987. Neglect of the remaining NSG (Barnett (1965) only lists  $g_{1-g_{50}}$  and  $g_{59-g_{62}}$  in his tabulation) can introduce an error no greater than  $2 \times 10^{-3}\%$  into the CI  $I_t(\mu)$  values. This error estimate is based on the observation that the sum of the eigenvalues for the complete 2-matrix expansion must be exactly  $(\frac{1}{2}) = 6$  with the normalization employed.

The 50 NSG used in the present computation of correlated  $I_t(\mu)$  values are of  $^1S$ ,  $^3S$ ,  $^1P$ ,  $^3P$ ,  $^1D$  or  $^3D$  symmetry.\* The NSG in turn are expanded in a sum involving two electron configurations built from STO's. Each configuration is an eigenfunction† of the spin and angular momentum operators  $\hat{S}^2$ ,  $\hat{S}_z$ ,  $\hat{L}^2$ ,  $\hat{L}_z$ . For instance a typical  $^1S$  NSG has the expansion

$$g_i(1,2) = \sum_t D_{(t)}(\mathbf{r}_1, s_1; \mathbf{r}_2, s_2) C_{tj} \quad (t = t_1, t_2) \quad (5a)$$

\* In § 2C of I it was mentioned that only the spatially symmetric and antisymmetric NSG components were needed to evaluate the  $I_t(\mu)$  expression, regardless of the  $M$  and  $S$  values of the atomic state. For singlet states such as we are examining here, the NSG are of either pure singlet or triplet character, and are equal to the natural geminals (NG) multiplied by an appropriate 2-particle spin function.

† The configurations listed by Barnett & Shull (1967) are defined only as to spin state. They must be projected in order to obtain the proper  $L$ -state (G. P. Barnett, private communication).

where the  $D_{(t)}$  notation indicates a configuration constructed from Slater type orbitals (STO)  $\varphi_{t_1}(\mathbf{r}, s)$ ,  $\varphi_{t_2}(\mathbf{r}, s)$  [cf. the notation of (21-I)]. Thus a  $^1S$  geminal can involve configurations of the form  $(np, mp)$ ,  $(nd, md)$ ,  $(ns, ms)$  and so forth. The  $s, p, d, \dots$  notation again indicates the symmetry species (angular momentum quantum number  $l$ ) of the single STO while  $n, m, \dots$  indicates its principal quantum number. In order to obtain  $^1S$  states from such configurations one can apply projection operator techniques (Fieschi & Löwdin, 1957; Calais & Linderberg, 1965). The  $^1S$  component of say a  $(3d, 3d)$  configuration can therefore be written as

$$(3d, 3d)_{1S} = 1/\sqrt{5} \{ [3d_{+2}\alpha(1) 3d_{-2}\beta(2)] + [3d_{-2}\alpha(1) 3d_{+2}\beta(2)] + [3d_0\alpha(1) 3d_0\beta(2)] - [3d_{-1}\alpha(1) 3d_{+1}\beta(2)] - [3d_{+1}\alpha(1) 3d_{-1}\beta(2)] \} \quad (5b)$$

where the notation is that used in (2b). As a specific example of 'diagonal' matrix elements [see (23-I)] encountered in the evaluation of  $I_t(\mu)$  we find that

$$\langle (3d, 3d)_{1S} | \exp\{i\boldsymbol{\mu} \cdot \mathbf{r}_{12}\} | (3d, 3d)_{1S} \rangle = |f_{3d(0)3d}|^2 + \frac{1}{7}|f_{3d(2)3d}|^2 + \frac{1}{7}|f_{3d(4)3d}|^2 \quad (5c)$$

where the  $f$ 's are exactly those defined by the expansion (24e) of I. Thus correlated  $I_t(\mu)$  values for  $\omega \neq 0$  were obtained by evaluating (23-I) with the truncated NSG expansion, subject to the constraint conditions (29a, b, and c) of I.

The accuracy of the present calculations was checked by a sum-rule procedure. The one-electron contributions to the potential energy of the scatterer can be obtained (Silverman & Obata, 1963) from the coherent X-ray scattering factor  $F(\mu)$  values with the sum rule

$$\int_0^\infty F(\mu) d\mu = \frac{\pi}{2} \left\langle \frac{1}{r} \right\rangle \quad (6)$$

while the two-particle contributions can be obtained (Tavard & Roux, 1965) from

$$\int_0^\infty \left[ \frac{I_t(\mu)}{I_{c1}} - N \right] d\mu = \pi \left\langle \frac{1}{r_{12}} \right\rangle. \quad (7)$$

Equations (6) and (7) were integrated numerically\* using a standard Simpson's rule procedure. The sum rule values of  $\langle 1/r \rangle$  and  $\langle 1/r_{12} \rangle$  are presented in Table 2 along with the values computed directly from the HF and Watson functions and from the NSO and truncated NSG expansions.

Table 2. Expectation values of  $\sum_i \frac{1}{r_i}$  and  $\frac{1}{2} \sum_{i,j} \frac{1}{r_{ij}}$  for the

$1S$ state of atomic Be			
	HF <sup>(a)</sup>	Watson <sup>(b)</sup>	Weiss <sup>(c)</sup>
$\left\langle \frac{1}{r} \right\rangle$ sum rule	8.4087	8.4178	8.4247
$\left\langle \frac{1}{r} \right\rangle$ calculated	8.4089	8.4179	8.4246
$\left\langle \frac{1}{r_{12}} \right\rangle$ sum rule	4.4892	4.4625	4.3803
$\left\langle \frac{1}{r_{12}} \right\rangle$ calculated	4.4896	4.4626	4.3803

(a) Computed from the analytical HF function of Clementi (1965).

(b) Computed from the two-configuration function of Watson (1961).

(c) Computed from the NSO and NSG analysis (Barnett, 1965) of A. W. Weiss (1961) CI function.

### 3. Discussion

No attempt is made to discuss the correlation problem *per se* since we are only interested in examining how the values of the total, coherent and incoherent scattered X-ray intensities are affected by electron correlation. Since the 2-matrix  $\Gamma^{(2)}$  is antisymmetric [see (7c) of I],

$$\Gamma^{(2)}(X_1, X_2 | X'_1, X'_2) = 0 \text{ if } X_1 = X_2 \text{ or if } X'_1 = X'_2,$$

where  $X_i = (\mathbf{r}_i, s_i)$  denotes the combined space-spin coordinate. Thus antisymmetry leads to an exchange correlation known as the 'Fermi hole' (Löwdin, 1959) which tends to keep electrons of parallel spin apart.

Let us now consider the case  $\mathbf{r}_1 \rightarrow \mathbf{r}_2$ . From the repulsive two-electron term  $H_{12} = e^2/r_{12}$  in the Hamiltonian  $H$  it is clear that  $H_{12}$  becomes increasingly large as  $r_{12}$  approaches zero. This mutual electron-electron repulsion introduces a 'correlation' or 'Coulomb hole' between the various electron pairs. For electrons of like spin, the correlation hole is partially compensated for by the Fermi hole. The Be HF function takes into account the indistinguishability of electrons (*i.e.* it is antisymmetric), but it does not yield any description of the correlation or Coulomb holes since

\* The sensitivity of the numerical integrations to the grid spacings  $\Delta\mu$  was checked by halving the spacings until the result was insensitive (one part in  $10^6$ ) to further scale division. Thus more  $F(\mu)$  and  $I_t(\mu)$  values were used in the numerical integrations than those which appear in Table 1, and these can be furnished on request.

there is no restriction on placing two electrons of opposite spin in the same (spatial) orbital.

If the charge distribution is spherically symmetric or if one averages over random orientations of a non-spherical atom, the effect of neglecting spatial correlation can be viewed in terms of the radial electron-electron distribution function,\* defined in the notation of Bartell & Gavin (1964) as  $P(r_{12})$ . As shown by Bartell & Gavin (1964, 1965),  $I_t(\mu)$  is then related† to the Fourier sine transform of  $P(r_{12})/r_{12}$ . It is expected that the introduction of spatial correlation *via* the Coulomb holes will cause a correlated  $P(r_{12})$  distribution to be more diffuse than its HF counterpart. Thus correlated  $I_t(\mu)$  values should be somewhat smaller in magnitude (for a given value of  $\mu$ ) than HF values provided that  $P^{\text{HF}}(r_{12})$  and  $P^{\text{corr}}(r_{12})$  are of the same general shape. In any event IPM (*e.g.* HF)  $I_t(\mu)$  values are expected to be somewhat in error since  $P(r_{12})$  determines  $I_t(\mu)$  and *vice versa*.

Gavin & Bartell (1966) have proposed a method for estimating the magnitude of correlation effects on  $I_t(\mu)$  values. According to Gavin & Bartell (1966), the total distribution function  $P(r_{12})$  can be defined as a sum of pair distribution functions  $P_{kl}(r_{12})$ , one  $P_{kl}$  for each pair ( $k, l$ ) of spin orbitals used in the construction of the wavefunction  $\Psi_g$ . As noted by Bartell & Gavin (1966) and others, the correlation energy  $E_{\text{corr}} = E_{\text{exact}} - E_{\text{HF}}$ , can be expressed as

$$E_{\text{corr}} = \frac{-Z}{2} \int_0^\infty \frac{\Delta D(r)}{r} dr + \frac{1}{2} \int_0^\infty \frac{\Delta P(r_{12})}{r_{12}} dr_{12},$$

where

$$\Delta D(r) = D_{\text{exact}}(r) - D_{\text{HF}}(r)$$

and

$$\Delta P(r_{12}) = P_{\text{exact}}(r_{12}) - P_{\text{HF}}(r_{12}).$$

In the notation of Bartell & Gavin,  $D(r)$  denotes the radial electron-nuclear distribution. With the assumption that  $\Delta D(r) \simeq 0$ , these authors obtain  $\Delta P_{kl}(r_{12})$  contributions from known pair correlation energies  $E_{kl}$  and

\* It is noted that  $P(r_{12})$  may be obtained from a general spin free 2-matrix

$$P^{(2)}(\mathbf{r}_1, \mathbf{r}_2 | \mathbf{r}_1, \mathbf{r}_2) = P_s(\mathbf{r}_1, \mathbf{r}_2 | \mathbf{r}_1, \mathbf{r}_2) + 3P_t(\mathbf{r}_1, \mathbf{r}_2 | \mathbf{r}_1, \mathbf{r}_2)$$

by the relation

$$P(r_{12}) dr_{12} = \iint P^{(2)}(\mathbf{r}_1, \mathbf{r}_2 | \mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

where the integration is carried out over all coordinates except  $r_{12}$ . In the present normalization

$$\int_0^\infty P(r_{12}) dr_{12} = \binom{N}{2},$$

the number of distinct electrons pairs. The Coulomb hole has been formally defined for two-electron systems by Coulson & Neilson (1961) which he generalize here as  $P_{\text{exact}}(r_{12}) - P_{\text{HF}}(r_{12})$ .

† The connection between the Bartell-Gavin (1964, 1965) formulation of  $I_t(\mu)$  for X-ray scattering from non-interacting gas atoms and the density matrix formulation derived in I is established in the Appendix of this paper.

then evaluate\*  $\Delta I_t(\mu) = I_t^{\text{exact}}(\mu) - I_t^{\text{HF}}(\mu)$  from the relation

$$\Delta I_t(\mu)/I_{cl} = \sum_k \sum_{l \neq k} \int_0^\infty \Delta P_{kl}(r_{12}) \frac{\sin(\mu r_{12})}{\mu r_{12}} dr_{12}.$$

Although Watson's (1961) function and the truncated NSG expansion of the Weiss 2-matrix do not exactly satisfy the virial theorem ( $\langle V \rangle / \langle T \rangle = -2.00163$  and  $-2.00022$ , respectively), the present computations clearly indicate that the correlation energy cannot be accounted for solely on the basis of an improved (relative to HF) radial electron-electron distribution function as assumed by Gavin & Bartell (1966). One must consider changes in the radial electron-nuclear distribution†  $D_0(r)$ . This fact is reflected in the expectation values  $\langle 1/r \rangle$  listed in Table 2 and in curves I and II of Fig. 2. Since the  $\Delta I_c(\mu)$  values are roughly twofold larger in magnitude than the  $\Delta I_t(\mu)$  values in the range  $0.0 - 0.3(\text{\AA})^{-1}$ , the assumption that  $D_0^{\text{HF}}(r) \simeq D_0^{\text{exact}}(r)$  is obviously not justified, and the accuracy of the Gavin-Bartell (1966) scheme for estimating  $\Delta I_t(\mu)$  values is also questionable. For example, Gavin & Bartell (1966) plotted a curve of estimated  $\Delta I_t(\mu)$  values for the  $1S$  ground state of Be (Fig. 3 of their paper) versus the scattering variable  $\mu$ . Their curve disagrees somewhat with curve I of Fig. 1 in that the positions of their maxima are shifted to slightly higher  $\sin(\omega/2)/\lambda$  values while their estimated  $L$ -shell peaking is roughly 25% higher than that indicated by the present calculations.

Gavin & Bartell (1966) also computed  $I_t(\mu)$  values from the CI wavefunction of Boys (1950) and from the analytical HF function of Roothaan, Sachs & Weiss (1960). Although the Boys function accounts for 52% of the correlation energy, these authors found negative values for  $\Delta I_t(\mu)$  (Fig. 3 of Bartell & Gavin, 1966). The implication of this result is that the Boys  $P(r_{12})$  distribution contracts relative to its HF counterpart over a certain range of  $r_{12}$  values (roughly corresponding to the  $K$ -shell region) indicating that this function does not yield a proper description of correlation effects.

In addition to providing 'accurate' X-ray scattering factors and intensities, the present computations yield qualitative information about the correlated electron-electron and electron-nuclear radial distributions

\* The Gavin-Bartell (1966) scheme is not rigorously correct since the  $\Delta P_{kl}(r_{12})$  functions which they obtain from known pair correlation energies  $E_{kl}$  are related to the second order transition density matrices  $\Gamma_{kl}^{(2)}(X_1, X_2 | X_1, X_2)$  whereas the  $I_t(\mu)/I_{cl}$  expression is defined in terms of the ground state wavefunction  $\Psi_g$ , or as has been shown in I, in terms of the spin-free 2-matrix obtained from  $\Psi_g$ . The pair correlation energies  $E_{kl}$  are defined as the transition matrix elements,  $E_{kl} = \langle \Phi_{\text{HF}} | H | \Phi_{kl} \rangle$ , where  $\Phi_{kl}$  is the sum of all determinants doubly excited with respect to the pair  $(k, l)$  in the HF determinant  $\Phi_{\text{HF}}$ . Using intermediate normalization, i.e.  $1 = \langle \Phi_{\text{HF}} | \Psi_{\text{exact}} \rangle$ , the total correlation energy  $E_{\text{corr}}$  is defined exactly as the sum of the  $E_{kl}$ 's for all possible doubly excited configurations.

† The function  $D_0(r)$  is defined in the Appendix.

$P(r_{12})$  and  $D_0(r)$ . It is observed from Fig. 2 that the  $K$ -shell component of the correlated  $D_0(r)$  distribution expands slightly towards larger  $r$  values while the  $L$ -shell component contracts considerably towards smaller  $r$  values, relative to the HF distribution. While the  $L$ -shell contraction is expected on the basis of an increased effective nuclear charge for the correlated atom, the slight  $K$ -shell expansion cannot be explained in this manner.

In order to determine whether or not these shifts in  $D_0(r)$  are due to 'pure correlation' effects (Larsson & Smith, 1969; Brown, Larsson & Smith, 1969) or to 'one-electron' effects (i.e. the one-electron contributions  $f_i$  discussed by Sinanoğlu & Tuan, 1963),  $I_c(\mu)$  values were computed with the 'best density' determinant\* constructed from the Weiss 1-matrix. The differences  $\Delta I_c(\mu)$  between HF and correlated and between 'best density' and correlated are shown in Fig. 3.

An expansion of the exact wavefunction  $\Psi_g$  in terms of the 'best overlap' orbitals\* has the property that it eliminates all singly-excited configurations, thereby allowing an exact assessment of 'one-electron' effects with respect to the expectation values of one-electron operators. From curve I of Fig. 2 it is evident that the  $L$ -shell contraction of the correlated  $D_0(r)$  distribution can be explained almost entirely on the basis of these effects. Although we base our conclusion on results obtained with the 'best-density' rather than the 'best-overlap' IPM, these two models (while not identical) are similar enough to account for the fluctuations in the correlated  $D_0(r)$  distribution observed here.

From Fig. 1 we can deduce that the maxima of the correlated  $P(r_{12})$  distribution are shifted towards higher  $r_{12}$  values, in agreement with the argument that the 'Coulomb holes' tend to make it more diffuse than the HF distribution. With respect to the Watson  $I_t(\mu)$  values, we see that the  $L$ -shell component of  $P(r_{12})$  shifts to higher  $r_{12}$  values while the  $K$ -shell component remains almost stationary with respect to HF. This behaviour is to be expected since the Watson function

\* A glossary of various IPM's is presented at the end of this paper.

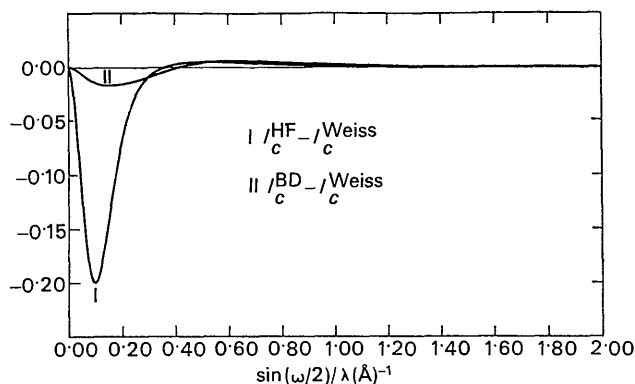


Fig. 3. Intensity differences for coherent scattering for the  $1S$  state of the Be atom.

was designed to take into account the near-degeneracy in the  $L$ -shell.

The largest differences between HF and CI values are observed for the incoherent intensity. Although the largest absolute deviation in  $I_i(\mu)$  is observed at  $0.105(\text{\AA})^{-1}$ , relative differences as large as 40–50% occur in the range  $0.0-0.020(\text{\AA})^{-1}$ . At these values of  $\sin(\omega/2)/\lambda$  the  $I_i(\mu)$  contributions to  $I_i(\mu)$  are indeed small relative to the coherent component  $I_c(\mu)$ , but any experimentalist making corrections for incoherent contributions to  $I_i$  must be aware of the fact that incoherent intensity values obtained from HF functions may be seriously in error at small values of the scattering variable.

#### 4. Summary

Correlated values for the total, coherent and incoherent intensities of X-ray radiation scattered by atomic systems can be obtained from the general density matrix formalism presented in I. Although values of the coherent scattering factor  $F(\mu)$  for the  $1S$  ground state of atomic Be are not presented here,\* they are easily obtained from the  $I_c(\mu)$  values listed in Table 1. The computation of  $I_c(\mu)$  values from the NSO expansion of the Weiss 1-matrix is much simpler than computing matrix elements of the scattering operator  $e^{i\mu \cdot \mathbf{r}}$  between the various determinants of the CI function. The latter procedure requires the evaluation of overlap integrals in addition to the matrix elements, whereas the NSO's are constructed mutually orthogonal.

The appreciable  $L$ -shell contraction of the correlated  $D_0(r)$  distribution can be explained by 'one-electron' effects, although a computation of  $I_c(\mu)$  values from the exact 'best-overlap' determinant will be required to unequivocally settle this point. Our  $I_c(\mu)$  computations have clearly demonstrated that  $D_0^{\text{HF}}(r) \simeq D_0^{\text{corr}}(r)$  is not a valid assumption. Conversely, the assumption that  $F_{\text{HF}}(\mu) \simeq F_{\text{corr}}(\mu)$  is not valid, as the accuracy of these values is clearly a function of the scattering variable  $\mu$ .

Finally, we wish to emphasize the importance and general utility of the sum rules (6) and (7) which were used to check the present calculations. Determinations of  $\langle 1/r \rangle$  and  $\langle 1/r_{12} \rangle$  by direct integration of experimental gas scattering intensity curves should yield reasonably accurate experimental values for the 1- and 2-electrons contributions to the correlation energy of

\* R. J. Weiss (1966) has reported correlated  $F(\mu)$  values which were calculated directly from the CI Be atom wavefunction of A. W. Weiss (1961), but there is a slight disagreement with our  $I_c(\mu)$  values [ $F^2(\mu) = I_c(\mu)$ ]. As a check on the numerical accuracy of Barnett's (1965) NSO expansion,  $I_c(\mu)$  values were also calculated from the truncated NSG expansion of the Weiss 2-matrix and these values agree with the 1-matrix results. As the truncated NSG expansion yields a total energy within 0.0003 atomic units of the actual Weiss (1961) energy, the NSO and truncated NSG expansions must be of comparable numerical accuracy. Also, the table of  $F(\mu)$  values given on p. 187 of Weiss (1966) has its headings interchanged since HF should read 55 configuration interaction and *vice versa*.

gas atoms. In practise the sum rule procedure for obtaining energies is simpler than the Bartell-Gavin (1964) method, wherein one first Fourier transforms the intensity data to obtain experimental  $D_0(r)/r$  and  $P(r_{12})/r_{12}$  curves and then integrates these curves to obtain total energies via the virial theorem.

#### APPENDIX

The expression for the total intensity of scattered X-ray radiation was defined [see (20-I)] by the relation

$$I_i(\mu)/I_{c1} = N + 2 \iint P^{(2)}(\mathbf{r}_1, \mathbf{r}_2 | \mathbf{r}_1, \mathbf{r}_2) \times \exp\{i\mu \cdot \mathbf{r}_{12}\} d\mathbf{r}_1 d\mathbf{r}_2, \quad (\text{A1})$$

where  $P^{(2)}$  denotes the combination  $P^{(2)} = 3P_t + P_s$  of triplet  $P_t$  and singlet  $P_s$  spatial 2-matrices. If the electron distribution is spherically symmetric or if one averages over all orientations  $\alpha, \beta$  of the scattering vector  $\mathbf{S}$  for a fixed value of  $\sin(\omega/2)/\lambda$  (this is equivalent to averaging over random orientations of a non-spherical atom); insertion of the plane wave expansion for  $\exp\{i\mu \cdot \mathbf{r}_{12}\}$  into (A1) and integration over  $\alpha, \beta$  yields

$$\begin{aligned} \left\langle \frac{I_i(\mu)}{I_{c1}} \right\rangle &= \int_0^{2\pi} \int_0^\pi \frac{I_i(\mu)}{I_{c1}} - N \sin \alpha d\alpha d\beta \\ &= 2 \iint P^{(2)}(\mathbf{r}_1, \mathbf{r}_2 | \mathbf{r}_1, \mathbf{r}_2) j_0(\mu r_{12}) d\mathbf{r}_1 d\mathbf{r}_2 \\ &= 2 \int_0^\infty P_0(r_{12}) \frac{\sin \mu r_{12}}{\mu r_{12}} dr_{12}, \quad (\text{A2}) \end{aligned}$$

where  $P_0(r_{12})$ , the totally symmetric component (under spatial rotations) of the distribution  $P(\mathbf{r}_{12})$ , is obtained from a general  $P^{(2)}(\mathbf{r}_1, \mathbf{r}_2 | \mathbf{r}_1, \mathbf{r}_2)$  by the relation

$$P_0(r_{12}) d\mathbf{r}_{12} = \iint P^{(2)}(\mathbf{r}_1, \mathbf{r}_2 | \mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2, \quad (\text{A3})$$

where the integrations are carried out over all coordinates but  $\mathbf{r}_{12}$ .

The connection with the Bartell-Gavin (1964) expression for  $I_i(\mu)$  and the 2-matrix formulation of  $I$  is established by noting that the Bartell-Gavin (1964) radial electron-electron distribution function  $P(r_{12})$  mentioned in the text above is just that defined by (A3).

If one considers the spherical average  $\langle F \rangle$  of the coherent scattering factor  $F$ , which was defined by (16-I) as

$$F(\mu, \alpha, \beta) = \int \exp\{i\mu \cdot \mathbf{r}\} \bar{y}(\mathbf{r}) d\mathbf{r} \quad (\text{A4})$$

one obtains

$$\langle F(\mu) \rangle = \int_0^\infty j_0(\mu r) D_0(r) dr \quad (\text{A5})$$

where

$$D_0(r) = r^2 \int_0^{2\pi} \int_0^\pi \bar{y}(\mathbf{r}) \sin \theta d\theta d\phi \quad (\text{A6})$$



is the totally symmetric component (under spatial rotations) of a general charge density matrix  $\bar{\gamma}(\mathbf{r})$ . For a specific orientation of an aspherical gas atom both  $I_t$  and  $F$  obviously depend on the orientation as well as the magnitude of  $S$ . Thus (A5) and (A2) can be considered as special cases of the general formulae (A4) and (A1) respectively.

### Glossary of independent particle models

Independent particle model (IPM) wavefunctions describing an atomic state may be constructed according to various criteria as follows:

(1) The HF wavefunction is chosen as the best single determinant approximation to the exact wavefunction  $\Psi_g$  as determined from the energy variation principle. Thus  $\Psi_{\text{HF}}$  yields the best single determinant approximation to the total energy. However, if  $\Psi_{\text{HF}}$  is constrained to be an eigenfunction of the spin and angular momentum operators, it cannot in general be represented by a single Slater determinant.

(2) The 'best-overlap' (BO) determinant is constructed to maximize the overlap between itself and the 'exact' or reference wavefunction  $\Psi_g$ . An expansion of  $\Psi_g$  in terms of BO orbitals (extended in an arbitrary way to form a complete basis set) eliminates all singly excited configurations. Such a model is therefore suitable for assessing the importance of 'one-electron' correlation effects. This model is also known as the 'exact SCF' (Löwdin, 1962) theory and the BO orbitals are often referred to as 'Brueckner' orbitals.

(3) The 'best-density' (BD) determinant is constructed so that its Fock-Dirac density matrix is the best idempotent approximation to the 1-matrix  $\gamma_{\Psi_g}(X_1|X_2)$  corresponding to  $\Psi_g$ . It is constructed from the first  $N$  (ordered after decreasing magnitude of their occupation numbers) NSO's of  $\Psi_g$ . In general the BO and BD orbitals are not the same (Kutzelnigg & Smith, 1964).

Other IPM's not specifically mentioned in context with the present work include the 'spin-adapted best density' and 'symmetry-adapted best density' models. These are discussed in the work of Smith & Kutzelnigg (1968*a, b, c*) and Kutzelnigg & Smith (1964) along with the BD and BO models.

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