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Elastic and Inelastic Electron Scattering by He and Ne Atoms in Their Ground States*†

E. M. A. Peixoto,‡ C. F. Bunge,§ and R. A. Bonham

Department of Chemistry, Indiana University, Bloomington, Indiana 47401

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A study of elastic and inelastic scattering of electrons by He and Ne atoms in their ground states is made within the framework of the first Born approximation. For the elastic case a partial-wave analysis is also carried out. Properly correlated configuration interaction wave functions, and also Hartree-Fock wave functions, are used throughout. It is shown that for an accurate description of both elastic and inelastic scattering, a correlated wave function is essential. A table of elastic and inelastic electron scattering factors for the elements studied is given.

I. INTRODUCTION

Calculations of differential cross sections for atomic electron scattering and x-ray scattering have been the subject of many works.[1–10]

The problem can be divided into separate considerations of elastic and inelastic scattering. For the elastic part the failure of the first Born approximation has already been discussed,[9,11] especially at low energies and for atoms of large atomic number. In the latter case an improvement can be made by means of the partial-wave method. However, for the inelastic part of the scattered amplitude we may expect that the first Born approximation should provide a more suitable description.[12]

Besides improving the method for treating the scattering process, a refinement can also be made by using very accurate wave functions to describe the scatterer.[6–10] This is especially true for the inelastic part where the first Born approximation contains a term-dependent on the reduced second-order density matrix, this one being sensitive to electronic correlation. For He, Bartell and Gavin[12,13] and more recently Kohl and Bonham[7] and also Kim and Inokuti[10] have illustrated this fact: There is a 6% discrepancy between the inelastic scattering factors obtained by means of Hartree-Fock (HF) wave functions and those computed through the more exact treatment. The inelastic scattering factors are lower than those calculated from HF wave functions. The influence of electronic correlation on elastic scattering factors is small; however, properly correlated wave functions are to be employed when a careful comparison between theory and experiment is sought.

Current developments of experimental techniques in electron scattering[14] have made it possible to measure differential cross sections with an uncertainty of less than 0.1%. This error is far smaller than the magnitude of the corrections introduced by electronic correlation. Thus it is of interest to perform more accurate calculations in order to determine (a) the accuracy of the scattering theory, (b) agreement between various atomic fields and experiment, and (c) details of the electronic charge cloud such as the electron-pair correlation function $P(r_{ij})$.[12,15,16]

One of the ways to take into account electronic correlation into the wave function is by the method of configuration interaction (CI).[17] Recently, a properly correlated CI wave function for Ne has become available[18] and it has been used in this work together with a CI wave function for He.

In the next section the theory is presented for the calculations of both elastic and inelastic parts of the scattered amplitude. This is followed by a brief commentary on the wave functions employed. Finally, the results obtained by means of CI wave functions are compared with those derived from HF wave functions.

II. THEORY

A. First Born Approximation

In the framework of the first Born approximation, the total electron intensity scattered by atoms can be written as[12,19]

$$I_T(s)=|f^B(s)|^2+(4\beta_0/a_0^2s^4)S(s)\,, \tag{1}$$

where

$$|f^B(s)|^2=(4\beta_0/a_0^2s^4)[Z-F_x(s)]^2\,, \tag{2}$$

$$S(s)=Z-F_x^2(s)+\sum_{i\neq j=1}^{N}\sum^{N}\langle\Psi|e^{i\vec{s}\cdot\vec{r}_{ij}}|\Psi\rangle\,, \tag{3}$$

$$F_x(s)=\sum_{i=1}^{N}\langle\Psi|e^{i\vec{s}\cdot\vec{r}_i}|\Psi\rangle\,, \tag{4}$$

$$s=(4\pi/\lambda)\sin(\theta/2),$$

$$\beta_0=1-(v/c)^2 \quad\text{and}\quad a_0=0.529\,167\ \text{Å}\,,$$

The quantity $|f^B(s)$ is known as the scattered amplitude, $F_x(s)$ is the x-ray form factor, $S(s)$ is the inelastic scattering factor and Ψ is the many-electron wave function of the atom.

B. Partial-Wave Treatment

For the exact treatment of the elastic scattering problem, a partial-wave (PW) analysis is needed. The radial part of the Schrödinger equation is considered:

$$\frac{d^2\varphi_l(r)}{dr^2}+\left[k^2+2V(r)-\frac{l(l+1)}{r^2}\right]\varphi_l(r)=0, \quad (5)$$

where $\lim_{r\to 0}\varphi_l(r)=0$

and $V(r)$ is the static scattering potential given by

$$V(r)=-\frac{Z}{r}+\int\frac{\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d\vec{r}\,'$$

in which $\rho(\vec{r}\,')$ is the electronic density.

Equation (5) is solved numerically by outward integration from the origin using Noumerov's method.[20-22] The starting point for the integration of (5) is obtained by means of a series solution, and it is advanced from the origin as l increases in order to save computing time and to avoid the occurrence of excessively large numbers during the calculations.

The phase shifts η_l are obtained through Eq. (5) by matching the derivatives[21] of the numerical solution to those obtained from the exact solution of (5) when $V(r)$ is negligible. This allows us to define the asymptotic radial wave function

$$\varphi_l=j_l(kr)\cos\eta_l-n_l(kr)\sin\eta_l, \quad (6)$$

where $j_l(kr)$ and $n_l(kr)$ are the spherical Bessel and Neuman functions, respectively. The phase shift η_l is obtained with the help of Eq. (6). Further, the scattered amplitude is obtained from the expression

$$f(k,\theta)=\frac{1}{2ik}\sum_{l=0}^{\infty}(2l+1)(e^{2i\eta_l}-1)P_l(\cos\theta)\,. \quad (7)$$

The summation above is carried out in double precision arithmetic (25 digits in the CDC 3600 computer) down to values of $\eta_l\sim 10^{-7}$.

Although we have performed a nonrelativistic partial-wave treatment for the scattering process discussed here, we do take into account corrections for relativistic effects on the wave vector $\vec{k}$, and on the mass of the scattered electron. These are not negligible, especially when we consider scattering of electrons in the keV energy range.

C. CI Expansion

The total wave function Ψ is expanded as

$$\Psi=\sum_{K,p}\Phi_K{}^{(p)}a_{Kp}\,, \quad (8)$$

where

$$\Phi_K{}^{(p)}=O(L^2,S^2)\left[\sum_{\alpha=1}^{p}D_{K\alpha}b_{K\alpha}{}^{(p)}\right]$$

$$=\sum_{\alpha=p}^{n_K}D_{K\alpha}c_{K\alpha}{}^{(p)}\,. \quad (9)$$

In Eq. (9), $O(L^2,S^2)$ is a product of a spin-angular-momentum projection operator times an orbital-angular-momentum projector,[23] and it is taken to be idempotent. In the Slater determinant $D_{K\alpha}$, the α label the possible determinants in configuration K [a configuration is defined by the ordered set of all (i,l) numbers which participate in a given determinant]. The superscript p labels the elements of a degenerate set.[24] Each Slater determinant is made up of spin orbitals defined by

$$\Psi_{ilm_lm_s}=R_{il}(r)Y_{lm_l}(\theta,\phi)\xi_{m_s}(\sigma_s)\,,$$

where the Y's are normalized spherical harmonics in the Dirac phase convention,[25] and the ξ's are the usual spin functions α, β with eigenvalues $m_s=\pm\frac{1}{2}$. The set of functions $\{R_{il}\}$ is expanded in terms of normalized Slater-type orbitals (STO) S_{jl} with $j=1,\ldots,J(l)$:

$$R_{il}=\sum_{j}^{J(l)}S_{jl}a_{jli}\,, \quad (10)$$

$$S_{jl}=N_{jl}r^{(n_j+l)}e^{-Z_{jl}r}\,, \quad (11)$$

$$N_{jl}=\left(\frac{(2Z_{jl})^{2l+2nj+3}}{(2l+2n_j+2)!}\right)^{\frac{1}{2}}\,,$$

and we have further the orthonormalization condition

$$\int_0^{\infty}R_{il}(r)R_{jl}(r)r^2dr=\delta_{ij}\,.$$

D. Matrix Elements

The evaluation of $F_x(s)$ is straightforward. For the inelastic case we must consider the operator G

$$G=\int\sum_{i\neq j=1}^{N}\sum^{N}e^{i\vec{s}\cdot\vec{r}_{ij}}\,d\Omega_s\,, \quad (12)$$

where the integration is taken over the angular coordinates of $\vec{s}$. The operator G depends on the $\vec{r}_{ij}$ only but not on their orientations in space, and thus it commutes with L^2. Thus

$$[G, O(L^2, S^2)] = 0 .$$

The matrix elements $G_{KJ}{}^{(pq)}$ are given by [26]

$$G_{KJ}{}^{(pq)} = \langle \Phi_K{}^{(p)} | G | \Phi_J{}^{(q)} \rangle$$

$$= \sum_{\alpha=1}^{p} \sum_{\beta=q}^{n_J} b_{K\alpha}{}^{(p)} c_{J\beta}{}^{(q)} \langle D_{K\alpha} | G | D_{J\beta} \rangle, \quad (13)$$

and the "turnover" rule is applied in such a way that the number of matrix elements between Slater determinants is kept to a minimum. The evaluation of quantities like $\langle D_{K\alpha} | G | D_{J\beta} \rangle$ has long been established.[27] The problem is reduced to the computation of integrals of the type

$$I(ac|bd) = \int \Psi_a{}^*(1) \Psi_c(1)$$

$$\times \langle e^{i\vec{s}\cdot\vec{r}_{12}} \rangle d\Omega_s \Psi_b{}^*(2) \Psi_d(2) d\vec{r}_1 d\vec{r}_2 . \quad (14)$$

The exponential $e^{i\vec{s}\cdot\vec{r}_{12}}$ may be expanded in terms of spherical harmonics[28] and then Eq. (14) simplifies into the well-known expression given by Condon and Shortley[27]

$$I(ac|bd) = \delta(m_s{}^a, m_s{}^c) \sum_{k=0}^{\infty} c^k(l^a m_l{}^a, l^c m_l{}^c)$$

$$\times c^k(l^d m_l{}^d, l^b m_l{}^b) R^k(ac|bd) ,$$

where now $R^k(ac|bd)$ is defined by

$$R^k(ac|bd) = (2k+1) I^k(ac) I^k(bd) ,$$

$$I^k(ac) = \int_0^\infty R_{i_a l_a}(r) R_{i_c l_c}(r) j_k(sr) r^2 dr .$$

The c^k are Gaunt coefficients and may be obtained from Ref. 27, and $j_k(sr)$ is a spherical Bessel function.[29]

III. WAVE FUNCTIONS

The HF wave functions are those of Clementi's table.[30]

For He, we have constructed a 14-term CI natural orbital expansion[31] starting from the STO parameters given by Weiss.[32]

In the case of Ne we have considered a 65-term CI wave function (consisting of 1480 Slater determinants) which is a truncation of a more accurate one.[18]

The CI energies are −2.903 07 a.u. (He) and −128.8602 a.u. (Ne), respectively, i.e., 98% of the electronic correlation energy is accounted for in the first case, while about 85% is recovered in the second case.

A properly correlated CI wave function is one which is obtained in the following way: A complete CI expansion[33] [Eq. (8)], expressed in terms of a nearly optimum one-electron basis and ordered according to decreasing magnitude of its linear coefficients a_{Kp}, is truncated. This truncated expansion has an almost maximum overlap with the exact wave function, for the number of terms considered. The CI wave functions employed in this work satisfy very closely the criterion expressed above.[34]

IV. RESULTS

A. Inelastic Scattering

In Table I a comparison is made between inelastic scattering factors obtained from HF and CI wave functions. For small s values, between 1 and 6 Å^{-1}, a discrepancy of 6 to 12% in the inelastic scatter-

TABLE I. Inelastic scattering factors obtained from HF and CI wave functions.

He				Ne		
s (Å^{-1})	$S(s)$ HF (this work)	$S(s)$ CI (Ref. 7)	$S(s)$ CI (this work)	s (Å^{-1})	$S(s)$ HF (Ref. 6)	$S(s)$ CI (this work)
0.5	0.054 20	0.051 45	0.051 64	1.0	0.5326	0.4860
1.0	0.205 77	0.194 75	0.195 39	2.0	1.8009	1.6106
2.0	0.676 59	0.637 74	0.639 20	3.0	3.2452	2.8733
3.0	1.1550	1.0888	1.0902	6.0	6.4467	6.0397
5.0	1.7231	1.6519	1.6520	8.0	7.5073	7.2887
7.0	1.9149	1.8733	1.8726	10.00	8.0737	7.9801
10.0	1.9838	1.9703	1.9699	12.0	8.4137	8.3768
12.0	1.9941	1.9877	1.9877	15.0	8.7658	8.7529
20.0	1.9998	1.9992	1.9993	20.	9.2017	9.1915

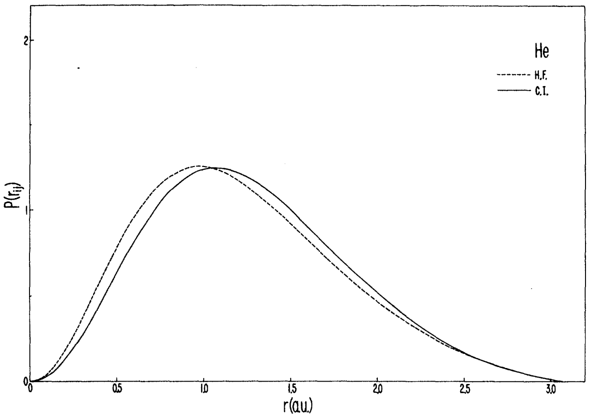

FIG. 1. Electron distribution function $P(r_{ij})$ for the ground state of He computed from a properly correlated CI (solid curve) and HF (dashed curve) wave functions.

ing factors for Ne is observed. That is, in the small s region, where inelastic scattering is predominant, the corrections to the total electron intensity due to electronic correlation are larger than today's experimental uncertainties.

It is illuminating to transform the two-electron terms in Eq. (3) into the electron-pair correlation function $P(r_{ij})$ discussed by Bartell and Gavin.[12,13] In Figs. 1 and 2 we plot $P(r_{ij})$ for He and Ne, respectively, computed with the CI and Hartree-Fock wave functions. These $P(r_{ij})$ values are obtained from the two-electron terms of (3) by means of a Fourier transformation which is carried out numerically using Filon's method.[35] In both cases the effect of the electronic correlation is to displace the peaks to larger distance. In the case of neon we can also see this effect for the K-shell electrons in the small shoulder $P(r_{ij})$ at $r \sim 0.2$ a.u. The effect of correlation in the $P(r_{ij})$ for He and Ne atoms is better seen in the plot of $\Delta P(r_{ij})$ (Figs. 3 and 4, respectively) as a function of r, where

$$\Delta P(r_{ij}) = P^{\text{CI}}(r_{ij}) - P^{\text{HF}}(r_{ij}). \tag{15}$$

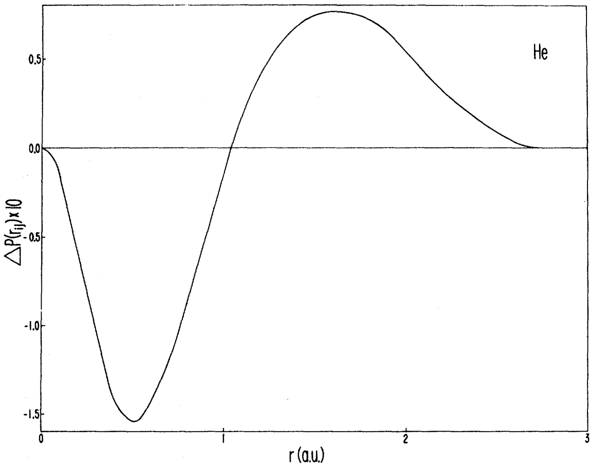

FIG. 3. $\Delta P(r_{ij})$ for He atom as defined by Eq. (15).

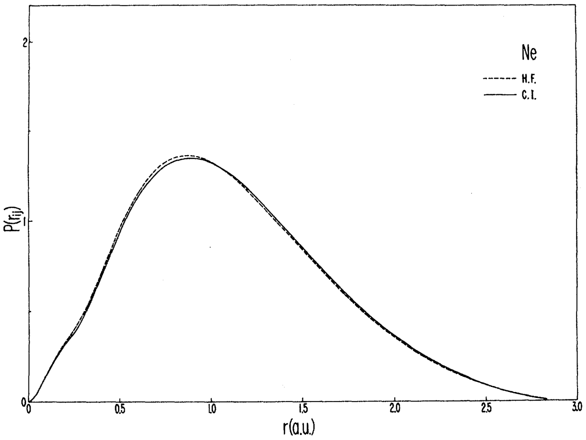

FIG. 2. The $P(r_{ij})$ function obtained using a CI wave function for the ground state of Ne (solid curve) compared with $P(r_{ij})$ calculated employing HF wave function (dashed curve). Notice the feature at $r \sim 0.1$ Å caused by the K-shell electrons.

In Tables II and III we list values for x-ray scattering factors and inelastic scattering factors calculated from properly correlated CI wave functions.

B. Elastic Scattering

It is the common opinion of many authors[36,37] that HF and properly correlated wave functions give essentially the same results for the values of one-electron properties. However, in elastic

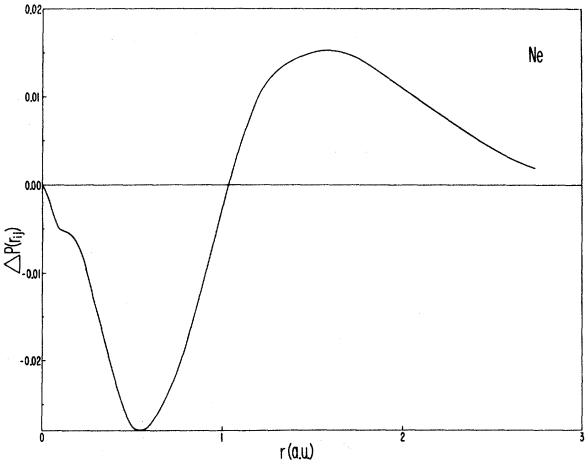

FIG. 4. $\Delta P(r_{ij})$ for Ne atom as defined by Eq. (15); the effect of the K-shell electrons can be seen at $r \sim 0.1$ Å.

TABLE II. X-ray scattering factor and total inelastic scattering factor for the He ground state.

s (Å^{-1})	$F_x(s)$	$S(s)$
1.00	1.8936	0.195 39
2.00	1.6250	0.639 20
3.00	1.2975	1.0902
4.00	0.992 27	1.4295
5.00	0.743 41	1.6520
6.00	0.553 72	1.7896
7.00	0.413 49	1.8726
8.00	0.310 95	1.9222
9.00	0.236 02	1.9520
10.00	0.180 98	1.9699
11.00	0.140 26	1.9809
12.00	0.109 84	1.9877
13.00	0.086 905	1.9919
14.00	0.069 432	1.9946
15.00	0.055 991	1.9963
16.00	0.045 551	1.9974
17.00	0.037 368	1.9982
18.00	0.030 895	1.9987
19.00	0.025 732	1.9991
20.00	0.021 580	1.9993
22.00	0.015 470	1.9996
30.00	0.005 012 7	1.9999

electron scattering, no rigorous attempt has been made to definitely prove this fact. In Table IV we compare results from "exact" partial-wave calculations employing HF and CI wave functions. The discrepancy is of the order of 0.7% for He and about 1.5% for Ne. This confirms the well-known fact that HF values for the electron density are qualitatively correct, although for accuracy at or below the 1% level, a properly correlated wave function is needed in order to describe the one-electron density.[38]

TABLE III. X-ray scattering factor and total inelastic scattering factor for the Ne ground state.

s (Å^{-1})	$F_x(s)$	$S(s)$
1	9.5774	0.486 01
2	8.4874	1.6106
3	7.1095	2.8733
4	5.7690	4.0688
5	4.6320	5.1390
6	3.7397	6.0397
7	3.0709	6.7512
8	2.5833	7.2887
9	2.2330	7.6860
10	1.9825	7.9801
11	1.8020	8.2024
12	1.6693	8.3768
13	1.5686	8.5201
14	1.4886	8.6432
15	1.4218	8.7529
16	1.3632	8.8532
17	1.3095	8.9463
18	1.2587	9.0334
19	1.2096	9.1150
20	1.1615	9.1915
21	1.1141	9.2629
22	1.0674	9.3294
23	1.0215	9.3910
24	0.976 31	9.4479
25	0.932 04	9.5002
26	0.888 84	9.5482
27	0.846 83	9.5920
28	0.806 10	9.6320
29	0.766 75	9.6683
30	0.728 83	9.7012

In Tables V and VI we list values for the partial-wave scattered amplitude and phase, as a function of s, for 40-keV electrons scattered by He and Ne atoms in their ground electronic state. The phase $\eta(s)$ is defined as follows:

TABLE IV. Partial-wave results for the scattered amplitude of 40-keV electrons employing HF and CI wave functions.

He				Ne		
s (Å^{-1})	$\vert f(s)\vert_{\mathrm{HF}}$ (this work)	$\vert f(s)\vert_{\mathrm{HF}}$[a,b]	$\vert f(s)\vert_{\mathrm{CI}}$ (this work)	s (Å^{-1})	$\vert f(s)\vert_{\mathrm{HF}}$[a]	$\vert f(s)\vert_{\mathrm{CI}}$ (this work)
0	0.4496	0.4509	.4526	0	1.750	1.777
1	0.4302	0.4309	0.4328	1	1.684	1.708
2	0.3801	0.3800	0.3819	2	1.510	1.528
3	0.3170	0.3168	0.3180	3	1.287	1.297
10	0.074 20	0.074 25	0.074 15	10	0.3234	0.3235
30	0.009 040	0.009 057	0.009 040	30	0.042 03	0.042 03

[a] Reference 9, see footnote 22.

[b] The difference between this column and the previous one arises because the authors of Ref. 9 have employed a least-squares technique in order to approximate the field, while in this work the potential was obtained directly from Poisson's equation.

$$\eta(s)=\tan^{-1}\{\mathrm{Im}[f(s)]/\mathrm{Re}[f(s)]\},$$

where Im and Re are the imaginary and real parts, respectively, of $f(s)$ as given by Eq. (7).

This work makes available for the first time elastic partial-wave and inelastic scattering factors for Ne based on a CI wave function giving 86% of the correlation energy. It is thus now possible to develop experimental sector corrections from Ne with nearly the same theoretical reliability as was previously possible with He. This is a major advance from the experimental point of view since neon intensities are considerably easier to measure than helium. In addition for very careful relative differential cross-section measurements of both elastic and total (elastic plus inelastic) scattering below the $\frac{1}{2}$% accuracy level, the results of this work should prove invaluable as a check of the first Born-scattering theory.

TABLE V. Partial-wave amplitude and phase for 40-keV electrons scattering elastically from the electronic ground state of He. The phases are given in radians. A CI wave function[31] was used.

s (Å^{-1})	$f(s)$ (Å)	$\eta(s)$
1	0.4328	0.022 54
2	0.3819	0.024 91
3	0.3180	0.028 74
4	0.2566	0.033 78
5	0.2048	0.039 73
6	0.1637	0.046 28
7	0.1319	0.053 16
8	0.1075	0.060 15
9	0.088 77	0.067 10
10	0.074 15	0.073 88
11	0.062 66	0.080 43
12	0.053 51	0.086 72
13	0.046 15	0.092 71
14	0.040 16	0.098 41
15	0.035 23	0.1038
16	0.031 13	0.1089
17	0.027 69	0.1138
18	0.024 78	0.1184
19	0.022 30	0.1228
20	0.020 17	0.1270
21	0.018 32	0.1310
22	0.016 72	0.1348
23	0.015 31	0.1384
24	0.014 08	0.1419
25	0.012 98	0.1452
26	0.012 01	0.1484
27	0.011 14	0.1515
28	0.010 37	0.1544
29	0.009 672	0.1573
30	0.009 040	0.1600

TABLE VI. Partial-wave amplitude and phase for 40-keV electrons scattering from the electronic ground state of Ne. The phases are given in radians. A CI wave function[18] was used.

s (Å^{-1})	$f(s)$ (Å)	$\eta(s)$
0	1.777	0.097 68
1	1.708	0.1008
2	1.528	0.1102
3	1.297	0.1253
4	1.067	0.1453
5	0.8663	0.1692
6	0.7012	0.1959
7	0.5701	0.2246
8	0.4672	0.2545
9	0.3867	0.2848
10	0.3235	0.3150
11	0.2736	0.3446
12	0.2338	0.3732
13	0.2018	0.4006
14	0.1758	0.4267
15	0.1545	0.4514
16	0.1368	0.4747
17	0.1220	0.4967
18	0.1096	0.5175
19	0.098 99	0.5371
20	0.089 88	0.5556
21	0.082 00	0.5731
22	0.075 14	0.5898
23	0.069 13	0.6056
24	0.063 83	0.6208
25	0.059 13	0.6353
26	0.5495	0.6491
27	0.051 20	0.6625
28	0.047 83	0.6754
29	0.044 79	0.6878
30	0.042 03	0.6999

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‡Rockefeller Foundation Predoctoral Fellow 1964–1968. Present address: Department of Chemistry, University of São Paulo, São Paulo, Brazil.

§Present address: Department of Chemistry, Universidade Central, Caracas, Venezuela.

[1] A. J. Freeman, Phys. Rev. 113, 169 (1959).

[2] International Tables for X-ray Crystallography, edited by N. F. M. Henry and K. Lonsdale (The Kynoch Press, Birmingham, England, 1962), Vol. 3.

[3] H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, Acta Cryst. 17, 1040 (1964).

[4] R. F. Pohler and H. P. Hanson, J. Chem. Phys. 42, 2347 (1965).

[5] D. T. Cromer, Acta Cryst. 113, 169 (1965).

[6] C. Tavard, D. Nicolas, and M. Rouault, J. Chim. Phys. 64, 540 (1967).

[7] D. A. Kohl and R. A. Bonham, J. Chem. Phys. 47, 1634 (1967).

[8] D. T. Cromer and J. B. Mann, J. Chem. Phys. 47, 1892 (1967).

[9] H. L. Cox, Jr., and R. A. Bonham, J. Chem. Phys. 47, 2599 (1967).

[10] Y. K. Kim and M. Inokuti, Phys. Rev. 165, 39 (1968).

[11] R. A. Bonham and T. Ukaji, J. Chem. Phys. 36, 72 (1962).

[12] L. S. Bartell and R. M. Gavin, Jr., J. Am. Chem. Soc 86, 3493 (1964).

[13] L. S. Bartell and R. M. Gavin, Jr., J. Chem. Phys. 43, 856 (1965).

[14] M. Fink and R. A. Bonham, private communications.

[15] P. Debye, Ann. Physik 46, 809 (1915); Z. Physik 24, 161 (1923).

[16] P. Debye, J. Chem. Phys. 9, 55 (1941).

[17] See, e.g. , J. C. Slater, Quantum Theory of Atomic Structure (McGraw-Hill Book Company, Inc., New York, 1960), Vol. 2.

[18] C. F. Bunge and E. M. A. Peixoto, "CI Wave Functions for the Ground State of Ne" (to be published).

[19] I. Waller and D. R. Hartree, Proc. Roy. Soc. (London) A124, 119 (1929).

[20] B. V. Noumerov, Monthly Notices Roy. Astron. Soc. 84, 592 (1924).

[21] M. A. Melkanoff, T. Sawada, and J. Raynal, in Methods in Computational Physics (Academic Press, Inc., New York, 1966), Vol. 6.

[22] E. M. A. Peixoto, Ph. D. thesis, Indiana University, 1968 (unpublished).

[23] P. O. Löwdin, Rev. Mod. Phys. 36, 966 (1964).

[24] For details concerning this paragraph, see A. Bunge, Ph. D. thesis, University of Florida, 1968 (unpublished); C. F. Bunge, Phys. Rev. 168, 92 (1968).

[25] $Y_{lm}^* = (-1)^m Y_{l,-m}$.

[26] P. O. Löwdin, Rev. Mod. Phys. 34, 520 (1962).

[27] E. U. Condon and G. H. Shortley, The Theory of Atomic Spectra (Cambridge University Press, Cambridge, England, 1963).

[28] See, e.g., R. G. Newton, Scattering Theory of Waves and Particles (McGraw-Hill Book Company, Inc., New York, 1966).

[29] For details concerning the evaluation of $I^k(ac)$ see Ref. 22.

[30] E. Clementi, Tables of Atomic Functions (San Jose Research Laboratory, IBM Corporation, San Jose, California, 1965).

[31] C. F. Bunge, work on He isoelectronic series (to be published).

[32] A. W. Weiss, Phys. Rev. 122, 1826 (1961); g-type orbitals have been excluded in our work.

[33] A CI expansion for which all possible configurations, with their complete degeneracies, have been considered.

[34] In order to be properly correlated, our wave functions have to be extended by including one g-type orbital and a few configurations associated with it.

[35] See, e.g., P. J. Davis and P. Rabinowitz, Numerical Integration (Blaisdell Publishing Co., Waltham, Mass., 1967).

[36] M. Cohen and A. Dalgarno, Proc. Phys. Soc. (London) 77, 748 (1961).

[37] J. Goodisman and W. Klemperer, J. Chem. Phys. 38, 721 (1963).

[38] See, e.g., O. Sinanoğlu, Advan. Chem. Phys. 6, 315 (1964).