

## Simple correlated wave functions for accurate electron densities: An application to neon

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We carry out a systematic study of the stability of the electron density in the ground state of neon upon adding well-defined improvements in the corresponding configuration-interaction (CI) wave functions. We describe a precise manner of obtaining a CI wave function which yields the electron density with an error no larger than 0.5% for a wide range of values of  $r$ . An accurate analytical density is obtained thereby, and a comparison with the Hartree-Fock density is made. Contrary to common belief, we find rather large discrepancies at  $r > 2$  bohrs between our accurate density and those obtained from two other CI wave functions, which account for more than 85% of the correlation energy.

## I. INTRODUCTION

It is generally accepted that Hartree-Fock (HF) wave functions provide electron densities which are accurate to about 1–5%,<sup>1,2</sup> as estimated from comparisons between HF electron densities and those obtained from x-ray scattering intensities<sup>3</sup> or calculated from more sophisticated wave functions.<sup>4–12</sup> It has been assumed that, for atoms of atomic number 10 or less, a wave function which includes over 80% of the correlation energy should probably be reliable to 0.1% in the density.<sup>1</sup> However, the obtaining of configuration-interaction (CI) wave functions which account for over 80% of the correlation energy is not trivial, and, at the same time, this requirement may be neither sufficient nor necessary.

Since the experimental accuracy in electron densities from electron and x-ray scattering is better than 0.1%,<sup>1</sup> it is important to obtain theoretical results to match this precision. Also, density functional theory requires accurate theoretical densities to construct accurate numerical exchange-correlation potentials<sup>13</sup> and to assess the accuracy of densities obtained from local-density approximations. Finally, because so many physical interpretations of the properties of atoms, molecules, and solids are based on densities obtained from HF wave functions, it is desirable to have definite estimates of the errors in the HF densities for the various regions of space.

Several ways of analyzing the effect of correlation on the electron density have been proposed.<sup>4–12</sup> All of them are directed toward a comparison of results for density-dependent properties calculated with HF and with correlated wave functions, assuming that highly correlated wave functions yield essentially correct results. Thus, Peixoto, Bunge, and Bonham,<sup>4</sup> who were mainly interested in obtaining elastic- and inelastic-scattering factors for Ne using a wave function accounting for 86% of the correlation energy, found that the HF results were 1.5% too low for elastic scattering [which depends on the one-electron density  $\rho(r)$ ]. Benesch and Smith<sup>8</sup> used a density-matrix formalism<sup>7</sup> to obtain values of the coherent, incoherent, and total scattered x-ray intensities

for the ground state of Be calculated from three different wave functions: a 55-term CI expansion, a two-term CI wave function, and an analytical HF function. They plotted differences between the intensities calculated from the various wave functions to examine the effects of electron correlation, observing an appreciable  $L$ -shell contraction of the one-electron density when correlation effects are included. In particular, they pointed out that the total intensity of scattered x-ray radiation from the Be ground state obtained by Gavin and Bartell<sup>9</sup> using a wave function accounting for 52% of the correlation energy was worse than the corresponding HF results. The above statement, however, was made under the implicit assumption that their 55-term CI wave function yielded the exact result.

Smith *et al.*<sup>10</sup> have also studied the effect of electron correlation on several other density-related properties. More recently, Beck<sup>12</sup> has calculated the electron density difference  $\Delta\rho(r) = \rho_{\text{corr}}(r) - \rho_{\text{HF}}(r)$  for Ne, using a 150-term CI wave function.

The only systematic study of the stability of the electron density as a function of the structure of the corresponding CI wave function was carried out by Bunge.<sup>14</sup> He calculated a sequence of increasingly accurate CI wave functions for Be tending toward his best  $\Psi$  (which accounts for 99.55% of the correlation energy), in order to assess the quality of several atomic properties and, in particular, the occupation-number spectrum of the natural orbitals. He obtained for the occupation numbers a stability better than 0.0001, except for the  $2s$  and  $2p$  orbitals which had occupation numbers still oscillating within 0.001 when his best  $\Psi$  was used.

Rather than studying the stability of the occupation numbers, we propose to study the stability of the density itself as a function of increasingly accurate CI wave functions until the density becomes stable within predefined limits of accuracy and within a certain range of values of  $r$ . Some of the specific questions we shall answer are (i) what are the types of configurations that are important for the density, (ii) are triple- and quadruple-excited configurations necessary at all, (iii) how large should the

TABLE I. Convergence of the density when  $d$ -type functions are added to the  $(6s\ 7p)$  basis in the  $L$  shell.

$r$ (bohrs)	$\rho_L$ [6,7] <sup>a</sup>	$\rho_L$ [6,7,1]	$\Delta\rho$ [(6,7,1)-(6,7)] (%)	$\rho_L$ [6,7,2]	$\Delta\rho$ [(6,7,2)-(6,7,1)] (%)	$\rho_L$ [6,7,3]	$\Delta\rho$ [(6,7,3)-(6,7,2)] (%)	$\rho_L$ [6,7,4]	$\Delta\rho$ [(6,7,4)-(6,7,3)] (%)
0.	7795.963	7795.224	-0.0095	7795.501	0.0036	7795.588	0.0011	7795.581	-0.00092
0.1	1089.338	1089.181	-0.014	1089.223	0.0038	1089.231	0.00070	1089.233	0.00019
0.2	181.897	181.795	-0.056	181.812	0.0092	181.811	-0.00058	181.813	0.0010
0.5	28.738	28.757	0.067	28.770	0.045	28.766	-0.015	28.767	0.0063
1.0	5.7024	5.7245	0.39	5.7227	-0.031	5.7197	-0.053	5.7193	-0.0070
1.5	1.0209	1.0187	-0.22	1.0195	0.083	1.0200	0.050	1.0198	-0.024
2.0	0.2038	0.2013	-1.27	0.2012	-0.023	0.2017	0.22	0.2017	0.013
2.5	0.04484	0.04379	-2.40	0.04363	-0.37	0.04376	0.29	0.04378	0.050
3.0	0.01061	0.01025	-3.44	0.01018	-0.76	0.01021	0.31	0.01022	0.068
3.5	0.002645	0.002536	-4.30	0.002509	-1.05	0.002518	0.33	0.002520	0.076
4.0	0.0006841	0.0006518	-4.95	0.0006439	-1.23	0.0006463	0.37	0.0006469	0.083
5.0	0.00004860	0.00004596	-5.74	0.00004537	-1.29	0.00004558	0.46	0.00004563	0.10
6.0	0.000003539	0.000003336	-6.07	0.000003296	-1.22	0.000003313	0.51	0.000003317	0.12

<sup>a</sup>Density obtained from a CI wave function containing all the single and double excitations of the  $L$  shell within the basis of  $6s$  and  $7p$  orbitals.

primitive basis of one-electron functions be, (iv) would only  $s$ ,  $p$ , and a few  $d$  Slater-type orbitals in the  $K$  and  $L$  shells be sufficient? We shall also define a systematic way of constructing density optimum wave functions, i.e., compact wave functions which yield electron densities within predefined limits of accuracy in a given range of values of  $r$ . As a test case we use the ground state of the Ne atom because the densities for two accurate wave functions<sup>4,12</sup> are available for comparison.

## II. METHOD OF CALCULATION

Nonrelativistic CI wave functions are calculated using an atomic CI program, DCI84, which is running on a Burroughs 7800 computer. The wave functions are expressed as

$$\Psi = \sum_{K,p} \Phi_K^{(p)} a_{Kp}, \quad (1)$$

where the  $\Phi_K^{(p)}$ 's are successively orthonormalized  $L^2$ - and  $S^2$ -symmetric projections of ten-electron Slater determinants  $D_{K\alpha}$  made up of orthonormal spin orbitals:<sup>15</sup>

$$\Phi_K^{(p)} = O(L^2, S^2) \sum_{\alpha=p}^{n_K} D_{K\alpha} b_{K\alpha}^{(p)}. \quad (2)$$

The spin orbitals are linear combinations of Slater-type orbitals (STO's) times a spherical harmonic, times a spin function:

$$\psi_{ilm_l m_s} = R_{il}(r) Y_{lm_l}(\theta, \phi) \xi_{m_s}(\sigma_s), \quad (3)$$

$$R_{il}(r) = \sum_j S_{jl}(r) a_{jli}, \quad (4)$$

$$S_{jl}(r) = N_{jl} r^{(n_j-1)} \exp(-Z_{jl} r). \quad (5)$$

Details of the method have been given elsewhere<sup>16</sup> and applied to several systems. The program DCI84 allows for a rather efficient optimization of STO parameters, and it permits the introduction of any type of configuration with one-electron harmonics up to  $l=7$ .

The one-electron reduced density matrix is calculated according to

$$\gamma(1, 1') = \sum_{i,j} \psi_i^*(1) \psi_j(1') \gamma_{ij}. \quad (6)$$

For a  $^1S$  state, the blocks of the density matrix are divided according to  $l$  values, since the block for  $\alpha$  spin is identical to the block for  $\beta$  spin and all blocks for different  $m_l$  values are equal to each other. In terms of the natural radial orbitals  $\chi_{il}(r)$ , the density for a  $^1S$  state may be written as

$$\rho(r) = 2 \sum_i (2l_i + 1) n_{il} \chi_{il}^2(r), \quad (7)$$

where

$$\chi_{il}(r) = \sum_j S_{jl}(r) c_{ji}, \quad (8)$$

and the  $n_{il}$ 's are the eigenvalues or occupation numbers of  $\gamma(1, 1')$ .

### III. ELECTRON DENSITY CALCULATIONS

Our aim is to obtain a wave function  $\Psi$  such that the electron density calculated from it does not vary appreciably upon further improvements in  $\Psi$ . The method of configuration interaction is especially suitable for this endeavor since one can always extend the basis set and check the stability of the density upon each addition of a new basis function.

As is well known,<sup>17</sup> for a given orbital symmetry and electron-correlation region ( $K$  shell or  $L$  shell in the case of Ne), successively energy-optimized STO's participate with decreasing energy contributions which moreover follow a definite pattern.<sup>18</sup> In this work we have observed that concomitant to an energy pattern of convergence there is a pattern of convergence for the electron density: successively energy optimized STO's expanding any of the major electron correlation regions yield smoothly decreasing contributions to the electron density. Thus the calculation of a density-optimized wave function follows the same steps as the calculation of an energy-optimized wave function, although the structures of the resulting STO sets are markedly different from each other.

We start from the self-consistent-field (SCF) orbitals of Clementi and Roetti,<sup>19</sup> supplemented by further orbitals which are obtained by successive orthogonalization within their  $6s$ ,  $4p$  STO basis. Next, we consider  $K$ -shell CI wave functions, i.e., CI expansions which include the reference configuration  $1s^2 2s^2 2p^6$  and all  $1s^2$  excitations. As a consequence of using  $K$ -shell CI expansions, the corresponding energy optimized STO's have mean values of  $r$  lying in the  $K$  shell region:

$$0 \leq \langle r \rangle = (n_j + \frac{1}{2}) / Z_{jl} \leq 0.3 \text{ bohr.}$$

New STO's are added in this way until the electron density changes no more than 0.1 % for  $r \leq 6$  bohrs. Then,  $L$ -shell CI wave functions are considered, i.e., CI expansions which include the reference configuration and all  $2s$ ,  $2p$ ,  $2s^2$ ,  $2p^2$ , and  $2s 2p$  excitations. The resulting energy optimized STO's have  $\langle r \rangle$  values between 0.5 and 1.7 bohrs.

We find that no extra STO of any  $l$  symmetry is useful to represent the density of a  $K$ -shell wave function better: percentual differences between densities calculated with and without any extra STO differ by less than 0.01 % for all  $r$ . In the  $L$  shell, however, we need to include  $p_5$ ,  $p_6$ ,  $p_7$ ,  $d_1$ ,  $d_2$ ,  $d_3$ ,  $f_1$ ,  $f_2$ , and  $g_1$  energy optimized STO's. Among these, the largest individual contribution corresponds to  $d_1$  (over 3 % at 3 bohrs, and as large as 6 % at 6 bohrs). The effect of the successive addition of  $d$ -type STO's to  $L$ -shell wave functions is shown in Table I.

It is interesting to emphasize that, although we optimize STO's according to an energy criterion, there is no relationship between their energy contribution and their importance in describing the electron density. For example,  $p_7$  only contributes about  $10^{-4}$  a.u. to the energy, yet its contribution to the electron density is almost 0.5 % between 3 and 4 bohrs. On the other hand, additional  $s$ ,  $p$ , or  $d$  orbitals in the  $K$  shell, or new  $d$  and  $f$  orbitals in the  $L$  shell, may contribute 50 times more to the energy and yet not be necessary for  $\rho$ .

A general idea of the convergence of the density can be obtained from Table II, where total densities at various stages of the calculation are given. These electron densities are obtained from wave functions which include all single and double excitations of the  $K$  shell,  $L$  shell, and intershell ( $1s 2s$  and  $1s 2p$  excitations) into the virtual orbitals. Such wave functions are denoted  $[a,b,c,\dots]$  where  $a,b,c,\dots$  are equal to the number of  $s,p,d,\dots$  STO's.

Our final STO set consisting of  $6s$ ,  $7p$ ,  $3d$ ,  $2f$ , and  $1g$  STO's is given in Table III. The corresponding  $[6,7,3,2,1]$  wave function is a 484-term CI expansion which should yield an electron density accurate to about 0.2 % for  $r \leq 6$  bohrs. [The total energy of our 484-term CI is  $-128.888\,004$  a.u. (Ne), slightly below the Bunge and Peixoto result on account of our  $\Psi$  having a  $g$  orbital (which they did not have) and in spite of the fact that our energy-optimized STO set was built with an electron-density-stability criterion rather than to obtain the lowest possible energy.]

Since our present computer code cannot handle the cal-

TABLE II. Convergence of the density as selected sets of energy optimized basis functions are added.

$r$ (bohrs)	$\rho_{\text{CR}}^a$	$\rho$ [6,7] <sup>b</sup>	$\rho$ [6,7,3]	$\rho$ [6,7,3,2]	$\rho$ [6,7,3,2,1]
0.	7792.988	7796.635	7794.426	7793.884	7793.625
0.1	1088.765	1088.987	1088.726	1089.001	1088.916
0.2	181.440	181.919	181.918	181.876	181.842
0.5	28.771	28.747	28.798	28.780	28.790
1.0	5.7969	5.7044	5.7228	5.7291	5.7323
1.5	1.0168	1.0209	1.0189	1.0192	1.0187
2.0	0.1937	0.2035	0.2007	0.2004	0.1999
2.5	0.04004	0.04463	0.04334	0.04307	0.04300
3.0	0.008900	0.01052	0.01007	0.009949	0.009954
3.5	0.002106	0.002618	0.002474	0.002484	0.002439
4.0	0.0005241	0.0006759	0.0006333	0.0006215	0.0006231
5.0	0.00003565	0.00004792	0.00004452	0.00004365	0.00004368
6.0	0.000002552	0.000003488	0.000003233	0.000003172	0.000003167

<sup>a</sup>Density obtained from the SCF wave function of Clementi and Roetti (Ref. 19).

<sup>b</sup>Density obtained from a CI wave function containing all single and double excitations of the  $K$ ,  $L$ , and intershell within the basis of  $6s$  and  $7p$  orbitals.

calculation of the electron density for the 484-term CI, we had to resort to various truncations of it. We considered three wave functions corresponding to the following truncations in the CI coefficients  $a_{Kp}$  of Eq. (1):  $|a_{Kp}| \leq 0.0003$ ,  $|a_{Kp}| \leq 0.0004$ , and  $|a_{Kp}| \leq 0.0007$ , yielding 330-, 300-, and 250-term CI expansions, respectively. The electron densities and density errors for these three wave functions are given in Table IV for certain values of  $r$ . Even a drastic truncation at  $|a_{Kp}| \leq 0.0017$  (yielding a 150-term CI) gives percentual density errors with respect to the best 330-term CI that do not exceed 2.1 % for  $r$  up to 6 bohrs.

The importance of triple and quadruple excitations was investigated. It was found that these excitations could be discarded altogether in the calculation of the electron density of Ne, as their effect is less than 0.01 % for all values of  $r$  considered.

Our analytical electron density, which has an error of about 0.1 % up to 3 bohrs and about 0.5 % between 3 and 6 bohrs, may be reproduced from Eqs. (7) and (8) using the occupation numbers and natural orbital expansion coefficients given in Table V.

The cusp condition for the electron density at the nucleus gives  $-(d\rho/dr)_{r=0}/2\rho(0)=10.05$ , which differs from the exact value of  $Z (=10)$  by 0.5 %.

#### IV. COMPARISON WITH THE HARTREE-FOCK DENSITY

A comparison between our best density  $\rho_{\text{best}}$ , the Hartree-Fock density, and two densities obtained from SCF wave functions is given in Table VI. We take  $\rho_{\text{HF}}$  from Beck.<sup>12</sup> Since  $\rho_{\text{HF}}$  is given as a numerical function in the radial mesh of Froese-Fischer,<sup>20</sup> we have obtained the other two densities in the same mesh for purposes of comparison.

The energies of the three independent-particle model wave functions<sup>12,19,21</sup> are practically equal among themselves, therefore, it is not surprising that the HF and the two SCF densities agree well with each other except for large values of  $r$ .

Our results show that between 0.6 and 1.4 bohrs the HF

TABLE III. STO set for  $\rho_{\text{best}}$ .

$j$	Type	$Z_{j\ell}$	Shell <sup>a</sup>
1	1s	9.484 86	<i>K</i> (SCF) <sup>b</sup>
2	1s	15.5659	<i>K</i> (SCF)
3	2s	1.961 84	<i>L</i> (SCF)
4	2s	2.864 23	<i>L</i> (SCF)
5	2s	4.825 30	<i>L</i> (SCF)
6	2s	7.792 42	<i>KL</i> (SCF)
1	2p	1.452 08	<i>L</i> (SCF)
2	2p	2.381 68	<i>L</i> (SCF)
3	2p	4.484 89	<i>L</i> (SCF)
4	2p	9.134 64	<i>L</i> (SCF)
5	3p	2.82	<i>L</i>
6	3p	7.45	<i>L</i>
7	4p	9.49	<i>L</i>
1	3d	3.625	<i>L</i>
2	3d	4.10	<i>L</i>
3	4d	3.90	<i>L</i>
1	4f	4.46	<i>L</i>
2	4f	4.90	<i>L</i>
1	5g	5.75	<i>L</i>

<sup>a</sup> Localized mainly in the shell as indicated.

<sup>b</sup> STO's of analytical self-consistent field orbitals (Ref. 19).

density is too high, in fair agreement with Beck.<sup>12</sup> In all other regions the HF density is too small, i.e., electron correlation produces a significant shift in the electron cloud from the  $r=0.6-1.4$  bohrs region, which corresponds to the inner and middle *L*-shell region, toward the *K* shell and the outer *L* shell regions.

TABLE IV. Analysis of errors introduced in the density upon different truncations of the final wave function.

$r$ (bohrs)	$\rho_{\text{best}}$ (330 CI)	$\rho$ (300 CI)	$\Delta\rho$ (330-300) (%)	$\rho$ (250 CI)	$\Delta\rho$ (330-250) (%)
0.	7793.625	7794.257	-0.0082	7793.817	-0.0025
0.1	1088.916	1088.981	-0.0065	1088.989	-0.0067
0.2	181.842	181.871	-0.016	181.871	-0.016
0.5	28.790	28.783	0.024	28.782	0.028
1.0	5.732 3	5.731 3	0.018	5.731 1	0.021
1.5	1.028 7	1.018 8	-0.011	1.019 0	-0.030
2.0	0.199 8	0.200 1	-0.10	0.200 1	-0.15
2.5	0.043 00	0.042 99	0.012	0.042 98	0.0046
3.0	0.009 954	0.009 930	0.23	0.009 920	0.34
3.5	0.002 439	0.002 430	0.39	0.002 425	0.57
4.0	0.000 623 1	0.000 620 4	0.43	0.000 618 9	0.67
5.0	0.000 043 68	0.000 043 56	0.26	0.000 043 43	0.57
6.0	0.000 003 167	0.000 003 166	0.04	0.000 003 156	0.35

TABLE V. Orbital expansion coefficients  $c_{ji}$  of Eq. (8) and occupation numbers  $n_i$  of Eq. (7) for the natural orbitals. The electron density is readily computed from this data through Eqs. (7) and (8).

s-type orbitals								
$j$	$s_1$	$s_2$	$s_3$	$s_4$	$s_5$	$s_6$		
1	0.936 189 82	-0.234 832 23	0.140 624 01	1.134 028 76	-0.747 975 83	-12.600 854 40		
2	0.048 980 82	-0.006 514 83	0.096 843 86	-0.103 855 94	-0.522 385 23	7.865 990 83		
3	0.000 856 74	0.201 938 36	1.174 030 51	-2.905 243 92	-3.526 517 58	-2.608 951 67		
4	0.002 123 12	0.645 919 38	0.184 147 00	4.440 559 55	7.366 041 24	6.522 478 94		
5	0.006 925 10	0.320 909 48	-2.018 481 73	-1.562 134 34	-7.702 816 98	-9.843 279 46		
6	0.019 412 39	-0.141 283 24	0.747 584 46	-1.267 946 54	4.810 528 56	11.726 039 36		
$n_i$	0.999 649 26	0.995 231 86	0.003 365 38	0.000 178 95	0.000 045 26	0.000 003 09		
p-type orbitals								
$j$	$p_1$	$p_2$	$p_3$	$p_4$	$p_5$	$p_6$	$p_7$	
1	0.236 691 42	0.728 461 68	-1.637 375 31	-1.880 490 52	-2.925 941 85	1.590 251 15	-0.840 308 08	
2	0.654 195 32	-0.980 200 23	23.977 507 16	25.748 899 70	42.390 640 00	-203.355 106 8	123.304 127 5	
3	0.277 326 85	-1.003 081 88	-9.441 676 02	-12.947 726 67	-32.152 379 88	104.522 706 7	-45.580 025 82	
4	0.024 505 61	0.051 456 91	0.321 978 01	2.935 320 07	1.043 026 88	-6.487 285 25	10.574 428 37	
5	-0.109 687 92	1.128 375 87	-16.474 697 46	-16.636 328 24	-26.285 282 24	148.805 240 5	-91.458 677 35	
6	0.005 242 71	0.204 625 01	1.523 506 29	0.443 294 73	20.638 102 08	-48.768 404 8	-43.542 059 54	
7	0.007 017 06	-0.002 686 01	-0.194 009 26	1.432 416 22	-4.402 491 77	14.674 028 62	42.346 548 05	
$n_i$	0.990 966 72	0.005 182 67	0.000 294 85	0.000 061 67	0.000 014 99	0.000 003 32	0.000 000 73	
d-type orbitals			f-type orbitals			g-type orbital		
$j$	$d_1$	$d_2$	$d_3$	$j$	$f_1$	$f_2$	$j$	$g_1$
1	3.507 456 01	-23.992 600 30	-199.418 735 1	1	1.333 273 54	-6.996 388 82	1	1.000 000 00
2	-1.683 478 72	17.497 247 38	125.734 870 7	2	-0.337 744 13	7.114 281 68	$n_1$	0.000 014 86
3	-0.877 779 10	7.014 254 52	78.073 983 99	$n_1$	0.000 179 00	0.000 023 45		
$n_1$	0.001 869 35	0.000 187 52	0.000 023 22					

TABLE VI. Comparison between  $\rho_{\text{best}}$ ,  $\rho_{\text{HF}}$ , and the densities from two SCF wave functions.

$r$ (bohrs) <sup>a</sup>	$\rho_{\text{best}}^b$	$\rho_{\text{HF}}^c$	$100\Delta\rho/\rho$	$\rho_{\text{SCF}}^d$	$100\Delta\rho/\rho$	$\rho_{\text{SCF}}^e$	$100\Delta\rho/\rho$
0.001 832	7512.823	7510.026	0.037	7512.277	0.0073	7514.529	-0.023
0.1	1088.916	1088.708	0.019	1088.765	0.014	1088.776	0.013
0.211 700	152.079	151.658	0.28	151.667	0.27	151.655	0.28
0.507 842	28.2092	28.1987	0.037	28.2018	0.026	28.1994	0.035
0.738 906	14.0994	14.2205	-0.86	14.2228	-0.87	14.2211	-0.86
1.009 964	5.5352	5.6015	-1.20	5.5973	-1.12	5.6013	-1.19
1.296 820	2.0347	2.0458	-0.55	2.0464	-0.58	2.0460	-0.56
1.564 263	0.8215	0.8160	0.67	0.8175	0.48	0.8161	0.48
1.772 542	0.4140	0.4066	1.79	0.4073	1.62	0.4066	1.79
2.008 554	0.1945	0.1884	3.14	0.1884	3.14	0.1884	3.14
2.579 034	0.033 97	0.031 69	6.71	0.031 43	7.48	0.031 70	6.68
3.110 909	0.007 255	0.006 469	10.8	0.006 432	11.3	0.006 477	10.7
3.994 486	0.000 632 4	0.000 509 1	19.5	0.000 532 0	15.9	0.000 500 8	20.8
5.129 021	0.000 031 11	0.000 021 48	30.9	0.000 025 33	18.6	0.000 019 15	38.4
6.186 781	0.000 001 940	0.000 001 184	39.0	0.000 001 561	19.5	0.000 000 881	54.6

<sup>a</sup>These are points from the mesh of Froese-Fischer (Ref. 20).

<sup>b</sup>This work.

<sup>c</sup>Reference 12.

<sup>d</sup>Calculated from the SCF wave function in Ref. 19.

<sup>e</sup>Calculated from the SCF wave function in Ref. 21.

TABLE VII. Comparison between densities obtained from different correlated wave functions.

$r$ (bohr) <sup>a</sup>	$\rho_{\text{best}}^b$	$\rho_{\text{BP}}^c$	$100\Delta\rho/\rho$	$\rho_{\text{Beck}}^d$	$100\Delta\rho/\rho$
0.001 832	7512.823	7510.980	0.024	7509.185	0.048
0.1	1088.916	1088.787	0.012	1088.830	0.0079
0.211 700	152.079	152.146	-0.044	152.127	-0.0032
0.507 842	28.2092	28.208	0.0035	28.194	0.053
1.009 964	5.5352	5.5292	0.11	5.5576	-0.40
1.564 263	0.8215	0.8235	-0.24	0.8235	-0.24
2.008 554	0.1945	0.1970	-1.29	0.1927	0.92
2.579 034	0.033 97	0.034 08	-0.32	0.032 71	3.70
3.110 909	0.007 255	0.006 842	5.69	0.006 701	7.64
3.994 486	0.000 632 4	0.000 467 7	26.0	0.000 528 4	16.4
5.129 021	0.000 031 11	0.000 013 76	55.8	0.000 022 31	28.3
6.186 781	0.000 019 40	0.000 000 475	76.4	0.000 001 23	36.6

<sup>a</sup>These are points from the mesh of Froese-Fischer (Ref. 20).

<sup>b</sup>This work.

<sup>c</sup>Obtained from the wave function of Bunge and Peixoto (Ref. 22).

<sup>d</sup>Reference 12.

Near the nucleus,  $\rho_{\text{HF}}$  and  $\rho_{\text{best}}$  agree to within the uncertainty in the latter. Only at about 0.2 bohr there is a significant discrepancy of 0.3% which, in principle, should be experimentally detectable. The relative drop in electron density at the onset of the  $L$  shell should also be amenable to experimental verification.

At large distances, we find that the HF density differs from  $\rho_{\text{best}}$  much more than predicted by Beck.<sup>12</sup> While at 3 bohrs there is already a 10% difference, the difference between  $\rho_{\text{best}}$  and  $\rho_{\text{HF}}$  continues to increase steadily to almost 40% at 6 bohrs.

## V. COMPARISON WITH CORRELATED NEON DENSITIES

Two other correlated neon densities were available to us: the one obtained from the wave function of Bunge and Peixoto<sup>22</sup> ( $\rho_{\text{BP}}$ ) and the one given by Beck<sup>12</sup> ( $\rho_{\text{Beck}}$ ). Both of them were obtained from wave functions which, like ours, account for about 85% of the correlation energy. All three densities are displayed in Table VII together with percentual differences between  $\rho_{\text{best}}$  and  $\rho_{\text{BP}}$  and between  $\rho_{\text{best}}$  and  $\rho_{\text{Beck}}$ . As in the preceding section, the electron densities are given in the radial mesh of Froese-Fischer.<sup>20</sup>

Contrary to common belief, the differences between these densities are not smaller than the differences between  $\rho_{\text{best}}$  and  $\rho_{\text{HF}}$  for the important region extending beyond 1.5 bohrs. As expected, there is good agreement between the three correlated densities in the  $K$  shell region.

In principle,  $\rho_{\text{Beck}}$  and  $\rho_{\text{BP}}$  should be amenable to improvement. However, since  $\rho_{\text{Beck}}$  is obtained from a wave function for which details, such as basis set, are not given, we cannot try and ameliorate it. Fortunately, the Bunge and Peixoto wave function is readily available to modifications. Using the technique developed in Sec. III we started, as Bunge and Peixoto did, from the nominal SCF basis of Bagus<sup>21</sup> and added new STO's as needed for the

convergence of the density, thereby obtaining an electron density in complete agreement with  $\rho_{\text{best}}$ , in spite of the fact that the two starting SCF densities differ markedly for  $r > 2.5$  bohrs. A comparison between the number of radial and angular one-electron functions needed to make up the energy optimum basis set of Bunge and Peixoto and the corresponding density optimum basis set, is given in Table VIII.

TABLE VIII. Comparison of the number of radial and angular one-electron functions between the energy optimum basis set of Bunge and Peixoto and a density optimum basis set, both obtained by starting from the Bagus SCF STO basis.

$l$	Shell localization	Number of STO's of $l$ symmetry in energy optimum basis set <sup>a</sup>	density optimum basis set <sup>b</sup>
0		4 (SCF)	4 (SCF)
	$K$	1	0
	$L$	1	0
1		3 (SCF)	3 (SCF)
	$K$	2	0
	$L$	1	4
2	$K$	2	0
	$L$	3	3
3	$K$	1	0
	$L$	3	2
4	$K$	0 <sup>c</sup>	0
	$L$	2 <sup>c</sup>	1

<sup>a</sup>Reference 22.

<sup>b</sup>This work.

<sup>c</sup>STO's added up in this work to those of Ref. 22.

## VI. CONCLUSIONS

We have found a quick and reliable way to obtain CI wave functions for the accurate calculation of the electron density of atomic systems over a wide range of values of the radial coordinate. By analyzing the stability of the density under well-defined improvements in the wave function, one can obtain a fair estimate of the error in the corresponding density at all  $r$  values. For the neon ground state, a CI wave function consisting of all single and double excitations formed in an orbital basis consisting of the SCF orbitals of Clementi and Roetti plus three  $p$ -, three  $d$ -, two  $f$ -, and one  $g$ -type energy-optimized STO's in the  $L$  shell, and with CI coefficients larger than 0.0005, yields a density which is stable within 0.5 % up to 6 bohrs.

In sum, the following points are to be noted from our results.

1. A stable electron density can be obtained by developing a density optimum basis set starting from a good SCF STO basis (for example, the widely available ones of Clementi and Roetti<sup>19</sup>) and adding energy optimized STO's with respect to well-defined wave functions spanning the physically relevant regions of space ( $K$  shell and  $L$  shell regions in the present example).

2. For Ne, HF, and good SCF wave functions yield densities showing good agreement among themselves while the electron density is noticeable, i.e., up to about 2 bohrs. The starting SCF STO basis does not appear to be critical to the stability of the final  $\rho$ , as supported by the fact that calculations starting from two different SCF STO sets yield  $\rho$ 's differing by less than 0.2 % even for large values of  $r$ , where the corresponding SCF densities differ by up to 30 %.

3. Most importantly, densities obtained from fairly correlated energy optimum wave functions (accounting for more than 80 % of the correlation energy) may be considerably in error: in the examples examined, significant errors in  $\rho_{BP}$  and  $\rho_{Beck}$  are observed for values of  $r$  greater than 2 bohrs.

The procedure developed here is being applied to all ground states of atoms from Li through F.

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