Electronic Wave Functions for Atoms. IV. Ground State of Ne[†]

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The configuration-interaction (CI) method is employed in an exhaustive investigation of the ground state of Ne. A 231-term CI expansion (formed from a determinantal space of dimension 5343), obtained with an optimized $6s6p5d4f$ basis, gives an energy $E = -128.8868$ a.u. (Ne). The Ne wave function is compared with those of Ne^{6+} and Ne^{8+}. A quantitative assessment of all sources of truncation errors is given. The nonrelativistic energy is estimated to be -128.932 ± 0.008 a.u. (Ne), in agreement with previous estimates obtained by different methods. Three- and four-excited determinants are shown to contribute 1% of the correlation energy. The L-shell correlations are shown to be nonadditive. Also, about 8% of the correlation energy is given by configurations containing g, h, and higher harmonics.

INTRODUCTION

A powerful approach to atomic configuration-interaction (CI) calculations has been recently discussed.[1] This work, on the Ne ground state, is one of a series of investigations on correlation effects in first-row atoms.[1-4]

I. CALCULATION

A. Slater-Type Orbital Basis

The Slater-type orbital (STO) basis, given in Table I, has been determined by a method previously discussed.[5] Many of the orbital exponents in Ne are related to those of C by a factor of $1.7 \approx Z_{Ne}/Z_C$, for equal r powers. Rough estimates for the energy errors due to the truncation of the STO set are as follows: -0.0017 ± 0.0005 a.u. for p_1^2 excitations, -0.0022 ± 0.0011 a.u. for $s_2 p_1$ excitations and -0.0006 ± 0.0002 a.u. for s_2^2 excitations; these are calculated from crude patterns of convergence obtained in a manner described elsewhere.[6] For the K shell, it is found that the energy of a Ne^{8+} wave function computed with our $6s6p5d4f$

basis is 0.002478 a.u. higher than Pekeris's[7]; this energy difference can be separated into 0.0008 a.u. due to g, h, and higher orbitals,[6] and 0.0017 a.u. due to the truncation of our $spdf$ STO set.

B. One-Electron Basis

The one-electron basis, given in Table II, consists of approximate $(s_2^2)(s_2 p_1)(p_1^2)$ pair natural spin orbitals (pair NSO's)[8] plus a set of orthogonalized K-shell STO's. No tail NSO's[8] are computed because the K-shell basis is small. Moreover, the use of KL-shell NSO's[2,5] is not appropriate here for two reasons: (i) the slow convergence of the L-shell CI expansion, and (ii) the negligible energy contributions of the KL-shell triple and quadruple excitations.

C. Subclasses

Any particular term of the CI expansion $\Phi_K^{(p)}$ is defined by[2,5]

$$\Phi_K^{(p)} = O(L^2, S^2) \sum_{\alpha=1}^{p} D_{K\alpha} b_{K\alpha}^{(p)} = \sum_{,\alpha=p}^{n_K} D_{K\alpha} c_{K\alpha}^{(p)} , \qquad (1)$$

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ᵃTABLE I. STO basis.

j	nl^a	Z_{jl}	Shell^b
1	1s	14.319	K (HF)^c
2	1s	9.224	K (HF)
3	3s	5.619	L (HF)
4	2s	2.518	L (HF)
5	2s	1.900	L
6	2s	19.000	K
1	2p	6.620	L (HF)
2	2p	3.484	L (HF)
3	2p	1.766	L (HF)
4	3p	3.920	L
5	2p	15.000	K
6	3p	19.000	K
1	3d	4.300	L
2	4d	3.625	L
3	5d	4.950	L
4	3d	21.000	K
5	4d	23.000	K
1	4f	4.600	L
2	5f	4.800	L
3	4f	3.800	L
4	4f	28.000	K

ᵃThe usual (nl) notation is employed, where $n = n_j + l + 1$.
ᵇLocalized mainly in the shell indicated.
ᶜThe Hartree-Fock (HF) STO's are those of Bagus (unpublished) [reproduced by A. D. McLean and M. Yoshimine in Tables of Linear Molecule Wave Functions (San Jose Research Laboratory, IBM Corporation, San Jose, Cal., 1967)].

where $O(L^2, S^2)$ is the usual projection operator for L^2 and S^2, and the α's label the different determinants $D_{K\alpha}$ belonging to configuration K.

A class is defined by a particular partition of N (number of electrons) among the spin orbitals with different values.[2] Within each class, a subclass is defined by a particular (ordered) set of partitions of the quantum number i among the spin orbitals with the same l value. (The "quantum number" i labels the one-electron functions with given l, m_1, and spin values.)

The terms $\Phi_K^{(p)}$ within a given subclass are characterized by the same set of $b_{K\alpha}^{(p)}$ and $c_{K\alpha}^{(p)}$ coefficients.[9]

D. Search For Terms

The steps in the configuration search are similar to those used for C,[5] and they are summarized in

Table III. Our 233-term K shell plus intershell expansion (fourth row in Table III), which already carries a -0.00007-a.u. truncation error, is further truncated in -0.0007 a.u., and it is combined with our best L-shell expansion, also truncated in -0.00034 a.u., to give the final wave function with an over-all truncation error of -0.0011 a.u. plus -0.0019 a.u. from certain L-shell triple and quadruple excitations (Sec. I E). The $spdf$-energy limit for the full CI is estimated at -128.897 ± 0.002 a.u. (Ne).

E. Wave Function

Our final wave function for Ne (WF1) consists of 231 terms formed from a determinantal space of dimension 5343. Its energy is $E = -128.88681$ a.u. (Ne). The eigenvector component of the Hartree-Fock (HF) configuration is 0.98362. The rest of the wave function is subdivided into invariant spaces and is displayed in tables which may be obtained from the authors.

F. Triple and Quadruple L-Shell Excitations

The only triple and quadruple L-shell excitations in WF1 belong to subclasses containing also one- and two-excited configurations. The others were omitted due to lack of computer storage to accommodate new subclasses. They were investigated, however, in a configuration search in which the first 60 terms of WF1 plus five others with partial energies lower than -0.0010 a.u. were kept throughout. The energy of this reference 65-term CI expansion (WF2) is -128.86025 a.u. (Ne).[10] The results are displayed in tables which may be obtained from the authors.

The following excitations give negligible energy contributions: $(p_1)^3 \rightarrow (p_x)^2 f$, [210, 3]; $s_2(p_1)^2 \rightarrow (s_x)^2 s_y$ or $s_x(s_y)^2$, [6, 1]; $s_2(p_1)^2 \rightarrow s_x s_y s_z$, [18, 2]; $s_2(p_1)^2 \rightarrow s_x s_y d$, [54, 2]; $s_2(p_1)^2 \rightarrow s_x p_y f$, [162, 2]; $s_2(p_1)^2 \rightarrow s_x (f)^2$, [218, 4]; and $(p_1)^4 \rightarrow s_x s_y (p_z)^2$, [74.3]. [The bracketed numbers indicate the number of determinants and degeneracies in the form (n_K, g_K).]

The over-all energy effect of triple and quadruple L-shell excitations in the Ne ground state is about -0.0037 a.u., of which -0.0018 a.u. are included in WF1. The $(s_1)^2(s_2)^2$ and $(s_1)^2(p_1)^2$ excitations carry energy contributions of -0.0002 and -0.0001 a.u., respectively. Thus, triple and quadruple excitations in Ne contribute about -0.0040 a.u. to the energy, i.e., 1% of the correlation energy (41 terms are needed in order to account for -0.0035 a.u., and more than 200 for the next -0.0005 a.u.). This result is believed to be definitive.

TABLE II. Orbital expansion coefficients in terms of STO basis.

s-type orbitals

j	s_1	s_2	s_3	s_4	s_5	s_6
1	0.08650002	−0.00431016	−0.07287025	−0.33238513	−3.24681777	−1.55678361
2	0.91716026	−0.24635131	−0.20039892	0.26859771	3.31176775	−4.08494266
3	0.00595000	0.29900940	1.62042963	2.91562917	−1.97113574	1.72036414
4	−0.00029000	0.76513849	−0.84993573	−7.97290541	2.92903190	−2.29811353
5	0.	0.	−0.65757132	5.72812225	−1.69872311	1.27838117
6	0.	0.	0.	0.	0.	5.48022296

p-type orbitals

j	p_1	p_2	p_3	p_4	p_5	p_6
1	0.08943933	−0.00898810	0.66112504	−6.01034295	−8.18970569	−6.45048230
2	0.50023626	1.78552907	−5.33967797	17.51566164	19.05607445	14.46558059
3	0.50721621	−1.28344032	−1.78563J⁴4	1.29310417	0.91470133	0.60600871
4	0.	−0.53676203	6.51609008	−14.40350689	−14.63884945	−10.92626108
5	0.	0.	0.	0.	2.18679955	−5.77527807
6	0.	0.	0.	0.	0.	7.33433259

d-type orbitals

j	d_1	d_2	d_3	d_4	d_5
1	0.49779673	−1.63612312	−1.72504629	−0.74284149	−0.96765942
2	0.67613944	2.10989210	−5.55574469	−0.92978442	−1.17084295
3	−0.12784176	−0.49690633	7.15572730	1.55089241	1.96679998
4	0.	0.	0.	1.04617314	−4.22264570
5	0.	0.	0.	0.	4.47061025

f-type orbitals

j	f_1	f_2	f_3	f_4
1	0.55572581	−3.72733574	1.21834391	−0.47639049
2	−1.42540115	1.56074336	−12.36742555	1.69455916
3	1.87479153	2.13785397	11.04999694	−1.25123713
4	0.	0.	0.	1.01159076

TABLE III. Steps in the configuration search.

Wave function	Number of terms	Energy	CI error[a] ($6s6p5d4f$)	Saturation[b] remainders	$spdf$-energy[b] limit
L shell: best expansion	234	−128.82788	−0.0019[c]	−0.0045	−128.8343
K shell: best expansion	45	−128.58545	−0.00001	−0.0017	−128.5872
K shell + $s_1 s_2$ excitations	127	−128.59069	−0.00001	−0.0019	−128.5926
K shell + intershell: best expansion	223	−128.61018	−0.00007	−0.0024	−128.6127
Final Wave Function (full CI)	231	−128.88681	−0.0030	−0.0069	−128.8967

[a]This is an estimated energy error due to the CI truncation, for our $6s6p5d4f$ basis.

[b]The entries in these columns are discussed in the text.

[c]Energy contribution from $(p_1)^3$, $s_2(p_1)^2$, and $(p_1)^4$ excitations of subclasses which do not give rise to singly and doubly excited configurations.

II. DISCUSSION

A. Correlation Energy

The correlation energy (CE) has been estimated previously: CE = − 0.390 a.u. (or, including the Lamb shift contributions into the correlation energy, CE = − 0.381 a.u.). [11] It shall be re-estimated here on the basis of our calculation and a study of the errors involved in the various truncations.

The difference between the CE of the K shell of Ne and that of Ne^{8+} is due to the same effects already discussed for C^5 and Be^2 (see Table IV). Thus, it is safe to assume that K-shell correlation energies can be computed in general to within 0.0002 a.u. by starting from the wave functions of the corresponding two-electron ion and the HF orbitals of the neutral atom under consideration, and taking into account all kinds of exclusion effects.

An estimate of the $spdf$-energy limit has been given in Table III. The energy effect of g, h, and higher harmonics for the K shell has been estimated in Sec. I A. For the L shell, and intershell, we look for patterns of convergence of the energy, as explained in Ref. 5. It should be remarked that we have been unable to detect such patterns within each invariant subspace. We believe this to be due (among other things) to the use of an orbital basis which is not appropriate to such a task. Further work in this direction is in progress.

The results for the L shell are given in detail in Table V. The nonrelativistic energy is estimated in Table VI.

TABLE IV. Comparison of K-shell correlation energies of Ne and Ne^{8+}.

	Ne	Ne^{8+}
E_0 [a]	− 128.54648	− 93.85169
K Shell CI [b]	− 128.58546	− 93.90433
$\Delta E = E - E_0$	− 0.03898	− 0.05264
Exclusion of s_2 and p_1		0.01015 [c]
$-\sum(s_1 s_x),\ s_x \neq s_2$		0.00366 [d]
Total exclusion effects = Exc		0.01381
$\Delta E + \mathrm{Exc}$		− 0.03883

[a] E_0 = energy of ground configuration.

[b] Obtained with our $6s6p5d4f$ basis.

[c] Computed as the energy difference between two full CI's for Ne^{8+} with and without orbitals s_2 and p_1.

[d] Computed by subtracting the corresponding partial energies relative to HF.

TABLE V. Diagram to estimate L shell Energy Contributions of g, h, and higher harmonics.

$d_1 = 1027$ [a]	$f_1 = 257$	$g_1 = 86$	$h_1 = 37$	$i_1 = 20$	$j_1 = 14$	$\geq k$
$d_2 = 228$	$f_2 = 66$	$g_2 = 26$	$h_2 = 16$	$i_2 = 10$	$j_2 = 8$	
$d_3 = 49$	$f_3 = 21$	$g_3 = 12$	$h_3 = 8$	$i_3 = 6$	$j_3 = 5$	
all others		12	8	7	6	
		136	69	43	33	50

Total (g, h, and higher) = 330 ± 60

[a] Energy contribution of orbital d_1, in units of 10^{-4} a.u.

B. Comparison of Ne and Ne^{6+} Wave Functions

A Ne^{6+} wave function was obtained with our $6s6p5d4f$ basis. Although the individual $(s_2)^2$ partial energies of excitations of the type $(s_2)^2 \to (p_x)^2$, $p_x p_y$; $(d)^2, d_x d_y$; $(f)^2, f_x f_y$ bear no relation whatsoever to those of Ne, a fortuitous cancellation of errors leads to approximately similar $(s_2)^2$ energy contributions, after taking care of the exclusion of p_1 in Ne. The relationship between the Ne and Ne^{6+}, $(s_2)^2 \to (s_x)^2$ and $s_x s_y$, excitations is totally obscured by the heavy mixture of the HF s_2 orbital in Ne^{6+} with s_2 and s_3 of Ne.

Contrary to what has been found to hold in the case of C, [12] the $s_1 s_2$ excitations of Ne and Ne^{8+} resemble each other only in a qualitative manner. As in C, the search for quadruple excitations of Ne^{6+} constitutes a foolproof method to discover the relevant $(s_1)^2 (s_2)^2$ excitations of Ne.

TABLE VI. Estimate of the total nonrelativistic energy.

$spdf$-energy limit	− 128.897 ± 0.002 [a]
Contributions of g, h, and higher orbitals to K shell	− 0.0008
Same, to L shell	− 0.033 ± 0.006
Same to $s_1 p_1$ excitations	− 0.001
Total (g, h, and higher)	− 0.035 ± 0.006
Total nonrelativistic energy	− 128.932 ± 0.008
HF energy	− 128.547 [b]
Correlation energy (estimate)	− 0.385 ± 0.008

[a] See Table III.

[b] E. Clementi, Tables of Atomic Functions (San Jose Research Laboratories, IBM Corporation, San Jose, Cal., 1965).

C. Comparison With Previous Work

Previous work has been reviewed recently by Nesbet. [13] The following analysis of his work is based on our results.

(a) Nesbet uses a $6s4p2d1f$ basis for the L shell. In view of our results, this basis should give a STO truncation error of (at least) -0.015 a.u. due to incompleteness of his $spdf$ basis (see Tables III and V) plus about -0.033 a.u. from g, h, and higher orbitals (see Table V). In other words, Nesbet's reported value for the CE of Ne is approximately 0.048 a.u. too high, from the point of view of the calculations involved. The fact that his computed CE almost coincides with the semiempirical estimates indicates that for Ne, an exhaustive second-order Nesbet-type calculation should give more than 110% of the CE.

(b) The comparison of results for $(s_1)^2$, s_1s_2, and s_1p_1 excitations is similar to the corresponding analysis for C, [12] in support of Nesbet's procedure of computing CE's in these cases.

(c) Nesbet's results for the L-shell CE are $e(2s, 2p) + e(2p, 2p) = -0.306435$ a.u. If we add to this value the -0.015 a.u. which we have estimated to be the truncation error in Nesbet's $spdf$ STO set, we get an $spdf$-energy limit: $[e(2s, 2p) + e(2p, 2p)]_{spdf} = -0.321$ a.u. This value should not differ substantially from the $spdf$ correlation energy limit of the full L-shell CI expansion. However, from Table III we see that $[CE(L \text{ shell})]_{spdf} = -0.288$ a.u., including triple and quadruple excitations. Thus, there is a 10% energy difference due to nonadditivity of the CE's of the individual spin orbital pairs, even after including the triple and quadruple excitations. [14, 15] This behavior probably arises because the three- and four-excited determinants in the L shell can be formed in several ways from different two-excited pairs *which occur with similar eigenvector components*, generating a sort of interference phenomenon. [For example, in the ground states of the four-electron isoelectronic series, the s_1s_2 excitations carry eigenvector components too small to interfere with the "products" of $(s_1)^2$ and $(s_2)^2$ excitations; in Be, additivity of $(s_1)^2$ and $(s_2)^2$ pair energies is satisfied to within 0.00001 a.u., after including the four-excited unlinked clusters. [2]]

In Table VII we give the partition of the calculated CE in terms of the ϵ parameters of HF orbitals and of pairs of HF orbitals, defined as the sum of the partial energies of the corresponding excitations.

After this work was completed, three new calculations were reported. [15–17] The work of Viers et al. is in perfect agreement with ours, their energy being a little bit higher due to their smaller one-electron basis set. Based on a perturbative

TABLE VII. Partition of the calculated correlation energy.

E_{HF} [a]	Energy
	-128.546481
$\epsilon(p_1, p_1)$ [b]	$-$ 0.193492
$\epsilon(s_2, p_1)$	$-$ 0.074422
$\epsilon(s_2, s_2)$	$-$ 0.010652
$\epsilon(s_1, p_1)$	$-$ 0.018552
$\epsilon(s_1, s_2)$	$-$ 0.004706
$\epsilon(s_1, s_1)$	$-$ 0.038469
$\epsilon(s_2)$	$-$ 0.000038
E(total)	-128.886812

[a]See Ref. [c] of Table I.

[b]Relative to Bagus's Hartree-Fock function.

analysis, Barr and Davidson[15] report an estimated -0.0056-a.u. energy contribution for the L-shell three- and four-excited determinants, which is of the same order of magnitude as our variational estimate of -0.0037 a.u. We believe the latter to be an upper bound with an error not greater than -0.0005 a.u., due to "interactions" between three- and four-excited determinants (this estimate of -0.0005 a.u. is based on effects observed while searching for the relevant L-shell three- and four-excited configurations). Nesbet[17] has recalculated his e_{ij} pair correlation energies with a nonoptimized basis set which includes harmonics up to $l = 6$; he finds that the sum of these computed pair correlation energies is 105.2% of the empirical CE. If our semiempirical analysis is correct (see Table V), an additional 2% of the CE should be obtained from harmonics with $l \geq 7$. The saturation remainders of Nesbet's STO basis have not been reported. Yet, the easiest check on Nesbet's procedure for calculating correlation energies is not to be made by adding higher harmonics, but rather by comparing his $spdf$-energy limits with those of a full CI calculation (see Sec. II C above).

D. Conclusions

This calculation turned out to be much easier than that of C, [12] regarding the size of the configuration search. Because we are dealing with a closed-shell state, the optimum partition of degenerate spaces cannot be tackled in the same way as for open-shell cases. [1, 5] Additional work on the partition of degenerate spaces is necessary for comparison with the ground states of Ne ions, and other first-row atom states.

The nightmare of three and four excitations is now removed, at least for atoms. But care must be exercised when interpreting Nesbet-type calculations: The three-body increments, as defined by Nesbet, may contribute substantially to the CE.

Two aspects should be distinguished in this paper: the rigorous one and the semiempirical one; of the latter, the most controversial step is the extrapolation of energy contributions of g, h, and higher harmonics (Table V), which, however, can be checked. [17] Obviously, it is impossible to avoid semiempiricism in calculations which do not yield the exact solutions. Rigorous lower bounds to the energy are useful in this connection, for purposes of verification.

Some expectation values for Ne have been computed, [10] others shall be reported soon, together with a study of their patterns of convergence.

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