

## CI-Hylleraas variational calculation on the ground state of the neon atom

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This calculation demonstrates that the combined configuration-interaction-Hylleraas (CI-Hy) variational method of Sims and Hagstrom can be applied to the  $^1S$  ground state of the neon atom. Coordinates  $r_{ij}$  have been included in the wave function so as to correlate explicitly the motion of all pairs of electrons in the atom. An energy of  $-128.8298$  hartree has been obtained from an 83-term wave function (73.5% of the correlation energy). An analysis of the pair correlation energies shows that it is more difficult to represent the electronic correlation in  $p$ - $p$  and  $s$ - $p$  pairs than  $s$ - $s$  pairs using Hylleraas functions. More experience with CI-Hy calculations on atoms containing as many as ten electrons is required before the method can compete with and give higher accuracy than the conventional CI calculations.

### I. INTRODUCTION

Recently, in a series of calculations, Sims and Hagstrom (SH) and coworkers have shown that a combined configuration-interaction-Hylleraas (CI-Hy) method is capable of giving very accurate values for the energies<sup>1,2</sup> and properties<sup>3</sup> of three- and four-electron atoms and ions. Furthermore, their results are superior to those obtained by other, more conventional methods such as configuration interaction. To our knowledge, at the present time, no variational calculations have been performed using Hylleraas-type wave functions on any system with more than four electrons; the main reason for this is that the many-electron integrals that arise are very cumbersome to evaluate. However, in the CI-Hy method the wave function is expanded in terms of configurations which are antisymmetric products of  $s$ ,  $p$ , or  $d$  orbitals with powers of just one  $r_{ij}$  coordinate, and the integrals for such calculations on any atom reduce to manageable forms which have been successfully dealt with in the very accurate SH calculation on beryllium.<sup>1,4</sup> The purpose of this work was to examine the general practicability of the CI-Hy method and to see if it was feasible to use the method in a calculation on the energy of the  $^1S$  ground state of the neon atom.

### II. CONFIGURATION-INTERACTION-HYLLERAAS METHOD

The CI-Hy method has been discussed in detail for a calculation on the  $^1S$  ground state of the beryllium atom.<sup>1</sup> For reasons of clarity we summarize the method here for a calculation on the  $^1S$  ground state of the neon atom. The wave function is of the form

$$\begin{aligned} \psi_{N_e}(X_1, X_2, \dots, X_9, X_{10}) \\ = \sum_K C_K \phi_K(X_1, X_2, \dots, X_9, X_{10}), \end{aligned} \quad (1)$$

where

$$\phi_K = \Theta(L^2) \Theta_{as} \left( \chi_1 r_{ij}^{\nu_K} \prod_{s=1}^{10} \bar{\theta}_{K_s}(\vec{r}_s) \right). \quad (2)$$

The power  $\nu_K$  of the interelectronic distance  $r_{ij}$  takes the values 0, 1, 2.  $\Theta(L^2)$  is an angular momentum operator and  $\Theta_{as}$  is an antisymmetrizing operator.  $\chi_1$  is the ten-electron spin function<sup>21</sup>

$$\begin{aligned} \chi_1 = (1/2^{5/2})(\alpha_1\beta_2 - \beta_1\alpha_2) \\ \times (\alpha_3\beta_4 - \beta_3\alpha_4) \cdots (\alpha_9\beta_{10} - \beta_9\alpha_{10}). \end{aligned} \quad (3)$$

The  $\bar{\theta}(\vec{r})$  functions are single Slater-type orbitals (STO's) of the form

$$\bar{\theta}(\vec{r}) = \{(2\xi)^{n+1/2}/[(2n)!]^{1/2}\} r^{n-1} e^{-\xi r} Y_{l,m}(\theta, \phi). \quad (4)$$

We follow the STO notation of Weiss.<sup>5</sup> The non-orthogonal basis set chosen in this work was  $1s, 2s, \dots, ns$  for the  $K$  shell [the notation meaning that each of these orbitals has the form (4), with  $l=0$ , and has the same exponent, which for neon was  $\sim 9.7$ ] and  $1s'', 2s'', \dots, ns''; 2p'', 3p'', \dots, np''$  for the  $L$  shell (the notation again implying that all of these orbitals have the same exponent, for neon  $\sim 2.925$ ).

Each configuration  $\phi_K$  is defined by the unique

$$F_K = r_{ij}^{\nu_K} \prod_{s=1}^{10} \bar{\theta}_{K_s}(\vec{r}_s) \quad (5)$$

part of Eq. (2). An example of such a configuration in the Weiss notation is  $r_{56}^2 1s^2 2s''^2 2p''^6$ , which corresponds to

$$\begin{aligned} \phi = \Theta(L^2) \Theta_{as} [\chi_1 r_{56}^2 1s(1) 1s(2) 2s''(3) 2s''(4) 2p''(5) \\ \times 2p''(6) 2p''(7) 2p''(8) 2p''(9) 2p''(10)]. \end{aligned}$$

$2p''_+, 2p''_0, 2p''_-$  have +1, 0, -1  $m$  quantum numbers, respectively. In accordance with the variation principle the minimum energy is found by finding the lowest root of the secular equations,

$$(\underline{H} - \underline{ES})\underline{C} = 0, \quad (6)$$

$$H_{KL} = \langle \phi_K | H | \phi_L \rangle, \quad (7)$$

$$S_{KL} = \langle \phi_K | \phi_L \rangle. \quad (8)$$

$H$  is the Hamiltonian of the system and  $\phi_K$  is defined in (1) and (2).

Upon integrating over spin functions [and noting that  $\mathcal{O}(L^2) = 1$  for all configurations used in this work] it can be shown that

$$H_{KL} = (1/10!) \langle A^R S^R F_K | H | S^R F_L \rangle, \quad (9)$$

$$A^R = \prod_{s=1}^2 \left[ \prod_{t=1}^4 \left( 1 - \sum_{u=t}^4 P_{2t+s-2, 2u+s} \right) \right], \quad (10)$$

$$S^R = \frac{1}{2^{5/2}} \prod_{t=1}^5 (1 + P_{2t-1, 2t}). \quad (11)$$

$P_{i,j}$  permutes the space coordinates of electrons  $i$  and  $j$ .  $F_K$  is defined in (5).

The restriction of only one  $r_{ij}$  coordinate per configuration leads to the result that  $H_{KL}$  and  $S_{KL}$  can be reduced to a linear combination of integrals of the following form:

$$G = \int F_{\text{corr}} \prod_{i=1}^{10} f_i(\vec{r}_i) d\vec{r}_i, \quad (12)$$

where  $f(\vec{r})$  is an STO and  $F_{\text{corr}}$  can be classified as one of only five different types,

$$r_{12}^s, r_{12}^s r_{13}^t, r_{12}^s r_{13}^t r_{23}^u, r_{12}^s r_{13}^t r_{14}^u, r_{12}^s r_{23}^t r_{34}^u, \quad (13)$$

where  $s$ ,  $t$ , and  $u$  are integers and take the values  $-1 \leq s, t, u \leq 4$ .

The restriction of including at most one  $r_{ij}$  factor in one configuration was first proposed by James and Coolidge<sup>6</sup> in their calculations on the lithium atom. This limitation is considered to be reasonable, since important standard correlating factors, which are products of "unlinked"  $r_{ij}$  variables, can, in the CI-Hy approach, be represented by a single  $r_{ij}$  factor and excited orbitals of the STO basis (for example, in the beryllium calculation<sup>1</sup>  $r_{12} 1s^2 2p''^2$  can represent the correlating factor  $r_{12} r_{34}^2$ ). Linked correlating factors, such as  $r_{12} r_{13}$ , have been shown to be energetically unimportant in a calculation on lithium,<sup>7</sup> but it is possible that such factors might have more importance for calculations on atoms such as neon which have more than two electrons in one shell. However, the inclusion of an  $r_{78} r_{89}$  factor in a calculation on neon would lead to integrals that would be exceptionally difficult to evaluate [for example,  $F_{\text{corr}}$  in (12) could then have the form  $r_{12} r_{23} r_{34} r_{45} r_{56}^2$ ].

A good stable scheme for evaluating the integrals defined in (12) and (13) which makes use of analyt-

ical techniques has been given in detail by SH,<sup>4</sup> and we found their expressions straightforward, if somewhat cumbersome to program.<sup>8</sup> Their formulas reduce the integrals to sums of products of Condon-Shortley coefficients,<sup>9</sup>

$$C^L(l', m'; l, m) = \left( \frac{4\pi}{2L+1} \right)^{1/2} \iint Y_L^{m'-m}(\theta, \phi) Y_l^{m'}(\theta, \phi) \times Y_l^m(\theta, \phi) \sin\theta d\theta d\phi \quad (14)$$

and simple cofactors and auxiliary integrals of the general form

$$X = \int_0^\infty x^f e^{-ax} dx \int_x^\infty y^g e^{-by} dy \times \int_y^\infty z^h e^{-vz} dz \int_z^\infty s^i e^{-6s} ds. \quad (15)$$

The auxiliary integrals can be evaluated using a series of recursion relationships.

### III. CALCULATIONS ON Be AND Ne

#### A. Beryllium

In order to thoroughly test the computer program written to calculate the integrals we reproduced (to nine significant figures) the energy of the first 25 functions (listed in Table III of Ref. 1) of the SH calculation on beryllium. This wave function included configurations of the form  $r_{34} 1s^2 2s''^2$ , and hence every type of integral that arises from the use of  $s$  and  $s''$  STO's was tested. Then the energy of the first four terms (from Table I of Ref. 11) which includes  $r_{12} 1s^2 2p''^2$  was reproduced (to all seven figures) to ensure that the program was correctly written for  $p''$  STO's.

We have some comments to add to the SH results.<sup>1</sup> First, we believe that for a limited set of CI-Hy configurations exponent optimization can have a more significant contribution to the energy than they suggested. For example, using the wave function (described by them in Table I of Ref. 1) which has the 11 configurations

$$\begin{aligned} &1s^2 3s'' 2s'', \quad 1s^2 4s'' 2s'', \quad 1s^2 5s'' 2s'', \\ &1s^2 6s'' 2s'', \quad 2s 1s 2s''^2, \quad 3s 1s 2s''^2, \\ &4s 1s 2s''^2, \quad 1s^2 2s''^2, \quad 1s^2 2s''^2 r_{12}, \\ &1s^2 2s''^2 r_{12}^2, \quad 1s^2 2s''^2 r_{34}, \end{aligned}$$

we obtained an energy of  $-14.647765$  hartree using the exponents  $\xi_s = 3.72$ ,  $\xi_{s''} = 1.08$  compared to their value of  $-14.644518$  hartree ( $\xi_s = 3.6847$ ,  $\xi_{s''} = 0.9562$ ). However, as the number of configurations is increased it is clear that the effect on

the energy of exponent optimization will diminish.

Secondly, it is of interest to note that the single configuration

$$\psi = \Theta_{\text{as}} [e^{-3.72(r_1+r_2)} r_3 r_4 e^{-1.08(r_3+r_4)} r_{34} \times \frac{1}{2}(\alpha_1\beta_2 - \beta_1\alpha_2)(\alpha_3\beta_4 - \beta_3\alpha_4)] \quad (16)$$

has a superior energy ( $-14.58455$  hartree) to the Hartree-Fock<sup>10</sup> energy ( $-14.57302$  hartree). This is because the Hartree-Fock method neglects the  $2s$ - $2p$  near-degeneracy, while the  $r_{34}$  factor introduces some  $p$  character (as well as electron correlation) in the  $L$  shell.

Once the integral program had been thoroughly tested, it was a relatively inexpensive operation to obtain a very-high-quality compact wave function for the ground state of beryllium. For example, we required about 30 min on the IBM 370/165 to obtain an energy of  $-14.66587$  hartree from a 40-term CI-Hy-type wave function ( $\sim 99.1\%$  of the correlation energy). This wave function is not published, because similar wave functions have been recently presented by SH.<sup>11</sup>

#### B. Neon: exponent optimization

For a calculation on the  $^1S$  ground state of the neon atom, it is clear from the above discussion that if a limited set of configurations are used it will be important to obtain good exponents for the  $1s, \dots, ns$  and the  $1s'', \dots, ns''; 2p'', \dots, np''$  basis sets discussed in Sec. II. However, exponent optimization using a set of configurations which include linear  $r_{ij}$  factors would be computationally very expensive, and consequently a small number of configurations which included single and double replacements from  $1s^2 2s''^2 2p''^6$  and terms which multiplied this ground configuration by  $r_{ij}^2$  factors were used. The optimum exponents obtained in this way were 9.760 for the  $ns$  basis set and 2.935 for the  $ns''$  and  $np''$  sets.

#### C. Neon: radial correlation

The beryllium calculations<sup>1,11</sup> show that configurations such as  $2s^2 2s''^2$  have a very significant contribution to the correlation energy even when  $r_{ij}$  variables are included in the wave function. Similar configurations, which account for radial correlation, will be particularly significant in the case of neon, because almost half of the pair correlation energy between electrons in  $p$  orbitals can be obtained,<sup>12</sup> in conventional CI calculations, by using configurations defined by excitations of the form  $p_2^2 \rightarrow p_i p_j$  (we define such configurations using the notation of Bunge<sup>13,14</sup>, noting that this excitation is equivalent to  $2p^2 \rightarrow ipjp$  in conventional

CI notation).

One advantage of the beryllium calculation was that the ground configuration  $1s^2 2s''^2$  had an energy ( $-14.5567$  hartree) which was reasonably close to the Hartree-Fock value<sup>10</sup> ( $-14.5730$  hartree), and a relatively small number of non-Hy-type configurations were required to obtain a value of  $-14.5883$  hartree, compared to the limiting value of  $-14.5911$  hartree,<sup>14</sup> which was calculated including only  $s$  orbitals in the basis set. A similar calculation was attempted for neon using configurations which were single and double excitations of the ground configuration  $1s^2 2s''^2 2p''^6$ , but 80 of these configurations yielded only half of the "radial correlation limit."<sup>12</sup> In contrast to the beryllium case, the ground configuration has an energy of  $-127.785$  hartree, which does not compare well with the Hartree-Fock<sup>15</sup> value of  $-128.547$  hartree, and it has been shown that<sup>15</sup> an extremely-high-quality basis set is required in a CI calculation on neon in order to obtain a significant amount of the correlation energy (we define the correlation energy as the difference between the Hartree-Fock energy and the exact eigenvalue of the nonrelativistic Schrödinger equation, noting that the "exact" value for neon has been estimated<sup>13</sup> to be  $-128.932$  hartree).

For these reasons we decided to account for most of the radial correlation by including a small selection of configurations in the wave function which were formed using the approximate natural orbitals of Bunge and Peixoto.<sup>13</sup> These were defined by excitations, from a near-Hartree-Fock ground configuration, of the form  $s_k^2 \rightarrow s_i s_j$ ,  $p_2^2 \rightarrow p_i p_j$ , and  $s_k p_2 \rightarrow s_i p_j$ , and 31 of these configurations (numbers 1-31 in Table I) accounted for  $\sim 34.39\%$  of the correlation energy and, we estimate,  $\sim 86\%$  of the radial correlation energy.<sup>12</sup> It must be stressed that no configurations were included in the ultimate wave function which were antisymmetrized products of  $r_{ij}$  variables with these natural orbitals, and consequently the most cumbersome integrals that involved the natural orbitals and which arose in the full calculation presented in Sec. IIID were of the form

$$\left\langle \prod_{i=1}^3 \Phi a_i(\vec{r}_i) r_{12} r_{13}^{-1} \prod_{i=1}^3 \Phi b_i(\vec{r}_i) \right\rangle, \quad (17)$$

where the  $\Phi a$  refer to natural orbitals and the  $\Phi b$  refer to single STO's. These "lop-sided" integrals can be evaluated relatively inexpensively. However, if the  $\Phi b$  were also natural orbitals the computer time required to evaluate all these integrals would be considerable; this problem is discussed in more detail in Sec. IV.

TABLE I. An 83-term CI-Hy wave function for neon, with energies for various selected truncations.

Term No. $n$	Term definition <sup>a</sup>	Energy $E(n)$ of $n$ -term function (hartree)	Term No. $n$	Term	Energy $E(n)$ (hartree)
1	$\phi_1$	-128.5465	51	$r_{15}$	
2-5	$s_1^2 \rightarrow s_i s_j, \dots$	-128.5569	52	$r_{19}$	-128.7944
6	$s_2^2 \rightarrow s_i s_i$	-128.5602	53	$r_{13}$	-128.7948
7-18	$p_2^2 \rightarrow p_i p_j, \dots$	-128.6491	54	$r_{12}^2$	-128.7959
19-24	$s_2 p_2 \rightarrow s_i p_j, \dots$	-128.6776	55	$r_{34}^2$	-128.7959
25-27	$s_1 p_2 \rightarrow s_i p_j, \dots$	-128.6781	56	$r_{78}^2$	
28	$s_2^2 \rightarrow s_2 s_i$	-128.6790	57	$r_{56}^2$	
29-31	$p_2^2 \rightarrow p_2 p_i, \dots$	-128.6790	58	$r_{910}^2$	-128.7993
32	$\phi_{32}$		59	$r_{59}^2$	
33	$r_1^2$		60	$r_{57}^2$	
34	$r_3^2$		61	$r_{79}^2$	-128.8014
35	$r_3^2$		62	$r_{37}^2$	
36	$r_5$		63	$r_{35}^2$	
37	$r_7$		64	$r_{39}^2$	-128.8140
38	$r_9$	-128.6797	65	$r_{17}^2$	
39	$r_{12}$	-128.7007	66	$r_{15}^2$	
40	$r_{34}$	-128.7063	67	$r_{19}^2$	-128.8168
41	$r_{78}$		68	$r_{13}^2$	-128.8182
42	$r_{56}$		69	$r_5 r_{59}$	
43	$r_{910}$	-128.7254	70	$r_9 r_{59}$	
44	$r_{59}$		71	$r_5 r_{57}$	
45	$r_{57}$		72	$r_9 r_{79}$	
46	$r_{79}$	-128.7775	73	$r_7 r_{57}$	
47	$r_{37}$		74	$r_7 r_{79}$	-128.8244
48	$r_{35}$		75	$r_5 r_{56}$	
49	$r_{39}$	-128.7890	76	$r_9 r_{910}$	
50	$r_{17}$		77	$r_7 r_{78}$	-128.8261
			78	$r_7 r_{37}$	
			79	$r_5 r_{35}$	
			80	$r_9 r_{39}$	-128.8282
			81	$r_7 r_{17}$	
			82	$r_9 r_{19}$	
			83	$r_5 r_{15}$	-128.8298

<sup>a</sup> The terms are collected into two main groups, and the notation used to define the configurations differs between the groups. Terms 1-31: Approximate natural orbitals classified by the excitations of particular orbitals from near-Hartree-Fock orbitals using the CI notation of Bunge.<sup>13,14</sup>  $\phi_1$  is the near-Hartree-Fock ground configuration (see Sec. III C). Terms 32-83: Classified by the  $R$  factor in  $\phi = \mathcal{O}_{as}(R\phi_{32}\chi_1)$ ,  $R = r_{ij}'' \prod_{s=1}^{10} r_s^n$ ,  $\phi_{32} \equiv 1s^2 2s''^2 2p''^6$  (see Sec. III D).

#### D. Neon: Hylleraas functions

The next step in the calculation was to add, to the 31-term wave function, configurations which were antisymmetrized products of single STO's with one  $r_{ij}''$  variable as defined in Eq. (2). For reasons of brevity in defining these configurations we decided to introduce a modification of the notation described in Sec. II. Every term in our wave function (other than numbers 1-31, Table I) can be written

$$\phi = \mathcal{O}_{as}(R1s(1)1s(2)2s''(3)2s''(4)2p_+''(5)2p_+''(6) \times 2p_0''(7)2p_0''(8)2p_-'(9)2p_-'(10)\chi_1), \quad (18)$$

$$R = r_{ij}'' \prod_{s=1}^{10} r_s^n. \quad (19)$$

Thus the  $R$  factor alone can define each configuration (for example,  $R = r_5 r_{56}$  corresponds to the configuration  $1s^2 2s''^2 3p_+'' 2p_+'' 2p_0''^2 2p_-'^2 r_{56}$  in the Weiss notation).

Fifteen of the configurations defined in (18) and (19) with  $R = r_{ij}''$  and 15 with  $R = r_{ij}^2$  were used so as to explicitly correlate all pairs of electrons in the atom. Furthermore, some "single" excitations of the ground configuration  $1s^2 2s''^2 2p''^6$  were included in the configuration set (e.g.,  $R = r_1^2$ ), since these terms have a behavior for large  $r$

similar to the corresponding  $r_{ij}$  factors, and previous calculations have shown that they have an important effect on the energy contributions from the  $r_{ij}$  variables.<sup>11,16</sup> The wave function thus formed contained 68 configurations and yielded an energy of  $-128.8182$  hartree ( $\sim 70.4\%$  of the correlation energy). The configurations are tabulated in Table I (numbers 32–68 correspond to those discussed in this section; the energy of the wave function formed from these configurations alone was  $-128.4778$  hartree).

After this a set of configurations which included configurations of the form  $R = r_i r_{ij}$  ( $5 \leq i \leq 10$ ) were added to the set (e.g.,  $r_9 r_{39}$ ) to attempt to represent the  $2p-2p$ ,  $2s-2p$ , and  $1s-2p$  correlation more accurately. The addition of nine such configurations gave only an extra  $3.1\%$  of the correlation energy, and the final result was  $-128.8298$  hartree ( $\sim 73.5\%$  of the correlation energy). The terms in the final 83-configuration wave function are displayed in Table I, along with the energies  $E(n)$  of the wave functions formed from various selected truncations (configurations 1– $n$ ).

#### IV. DISCUSSION

The results of the neon calculation do not reflect the success of the beryllium calculation. In that calculation<sup>1</sup> a limited set of configurations which correlate all pairs of electrons with  $r_{ij}$  and  $r_{ij}^2$  coordinates (terms 1–27, 63, and 69, Table II of Ref. 1), and which in this sense forms a set of configurations equivalent to that used in our full neon calculation, gave about  $87\%$  of the correlation energy of beryllium, compared to the value of  $73.5\%$  reported here for neon. To improve the neon wave function it will obviously be necessary to include further classes of CI-Hy-type configurations (such as those containing correlating factors  $R = r_i^2 r_{ij}$ ) in the set. However, an extensive search for the terms that will give important energy contributions is needed, and the computing time we would have required to do this would have been excessive. For this reason it is important for us to briefly outline our computational approach, with particular reference to the calculation of the many-electron integrals.

Consider a four-electron integral of the form

$$\left\langle \prod_{i=1}^4 \Phi c_i(\vec{r}_i) r_{12} r_{23} r_{34}^{-1} \prod_{i=1}^4 \Phi d_i(\vec{r}_i) \right\rangle, \quad (20)$$

where  $\Phi c$  and  $\Phi d$  refer to single STO's. If these integrals are stored in the conventional way used for two-electron integrals [labeling them by all eight STO's in (20)] then  $\frac{1}{16}[n_1^4(n_1+1)^4]$  integrals would be required ( $n_1$  is the total number of STO's

in the basis set), and about  $6.7 \times 10^6$  bytes would be needed to store all the integrals in single precision for the eight-orbital basis set ( $1s$ ,  $2s''$ ,  $2p_+''$ ,  $2p_0''$ ,  $2p_-''$ ,  $3p_+''$ ,  $3p_0''$ ,  $3p_-''$ ) used in this work. Consequently it would be impossible to store all the integrals in core, which is important for the fast generation of the matrix elements.

However, the magnetic quantum numbers can be effectively factorized out of the integral formulas<sup>4</sup> which can be expressed as sums of products of the Condon-Shortley coefficients defined in (14) (which can be introduced when the actual matrix elements are generated) with radial-type "reduced" integrals that depend on  $n'$ ,  $\xi'$ , and  $l'$  only.  $n'$ ,  $\xi'$ , and  $l'$  define functions of the form

$$r^{n'-1} e^{-\xi' r} Y_{l',0}(\theta, \phi), \quad (21)$$

which are themselves obtained (in linear combinations) from the multiplication together of two of the STO's in the basis set. The number of these reduced integrals that need to be evaluated and which correspond to those defined in (20) depends on  $n_2^4$ , where  $n_2$  is the total number of functions, defined in (21), which can be formed. For the basis set used in this work  $n_2 = 12$ , so that about  $8.0 \times 10^4$  bytes were needed to store all these particular integrals in single precision on the IBM 370/165 (the single-precision limitation gave at least seven-figure accuracy in the final energies). However, the computing time needed is particularly critical and the evaluation of the total number of integrals required for the generation of the matrix elements took about 140 min. An addition of a  $4p''$  function to the basis set (which raises  $n_2$  to 18) would not only prevent the storage of all the reduced integrals in core (maximum  $4.0 \times 10^5$  bytes on the IBM 370/165 at Cambridge University) but would result in an excessive 12 h of computer time being required to calculate all the integrals. It is thus clear that further investigations in the CI-Hy method are necessary, with particular reference to the development of programs and methods to efficiently calculate the three- and four-electron integrals before an extensive configuration search and a subsequent improvement in the neon energy reported here can be made.<sup>17</sup>

The configurations defined in Eq. (2) consisted of an  $r_{ij}^p$  factor multiplied by a "minimal basis set" configuration  $1s^2 2s''^2 2p''^6$  (or a single excitation of this term) in which the radial part of the  $p''$  functions have a poor functional form. It is probable that the replacement of this minimal basis set by Hartree-Fock orbitals would give better results, although the relatively small effect on the energy of including  $r_i r_{ij}$  factors in our calculation (the  $r_i$  part of which should contribute

TABLE II. Pair correlation energies (in hartrees) for neon calculated by the CI-Hy method and the Bethe-Goldstone technique.

Pairs <sup>a</sup>	This work	Bethe-Goldstone <sup>b</sup>
1s-1s	-0.032 34	-0.039 93
1s-2s	-0.001 56	-0.005 14
1s-2p	-0.013 65	-0.019 89
2s-2s	-0.008 68	-0.011 73
2s-2p	-0.061 73	-0.090 55
2p-2p	-0.161 53	-0.243 07
Total <sup>c</sup>	-0.279 49	-0.410 31

<sup>a</sup> See Sec. IV for discussion.

<sup>b</sup> Reference 15.

<sup>c</sup> Note that  $E(\psi_{12}) = -128.555\,96$  hartree.

to an effective improvement in the functional form of the  $p$  function) implies that it is doubtful that such a replacement would produce an exceptionally large improvement in the energy. Furthermore, the discussion above shows that we would require an enormous amount of computing time to evaluate the necessary integrals (for example, we would need about 120 h for such a calculation using the near-Hartree-Fock orbitals of Bunge,<sup>13</sup> noting that  $n_2$  as defined above would then be equal to 34).

In Table II a breakdown of the approximate "pair correlation energies" is given, divided into the six different types (1s-1s, 1s-2s, 2s-2s, 2s-2p, 2p-2p, and 1s-2p). These closely correspond to the "symmetry-adapted pair correlation energies" discussed in detail by Schaefer.<sup>18</sup> They were obtained by starting from a set ( $\psi_{12}$ ) of 12 configurations which included the near-Hartree-Fock configuration plus the single-excitation configurations (the effect on the energy of which is small when  $r_{ij}$  factors are not included in the wave function). Then the remaining configurations were divided into various classes corresponding to a particular pair correlation type (for example, a configuration containing an  $r_{37}$  factor contributed to 2s-2p correlation), and the resulting secular equations formed from  $\psi_{12}$  and all configurations of a certain class were solved. The energy of  $\psi_{12}$  was subtracted to give the pair correlation energy of the class in question. The pair correlation energies are approximately additive (adding the values for all the different pairs to the energy of  $\psi_{12}$  gives  $-128.8354$  hartree, compared to the 83-configuration variational result of  $-128.8298$  hartree). This result is somewhat surprising, considering that in a similar calculation on beryllium Perkins<sup>16</sup> determined that the 1s-1s and 2s-2s pair correlation energies were nonadditive by as much as 10%. The results of a Bethe-Gold-

stone<sup>15</sup> calculation (which, it must be noted, gives a slight overestimate of the correlation energy) are compared to our values in Table II. It is clear from these results that the CI-Hy method is relatively deficient in obtaining the large 2p-2p, 2s-2p, and 1s-2p pair correlation energies. The 1s-1s and 2s-2s values are reasonable, although the very small 1s-2s energy compares poorly.

To a certain extent the main conclusion that we infer from these pair correlation results, that the correlation in  $p$ - $p$  and  $s$ - $p$  pairs is comparatively poorly represented by Hylleraas functions, is partly reflected in the beryllium calculation<sup>1,11</sup> in which several more CI-Hy-type terms were needed to represent the  $L$  shell (which has some  $p$  character) and the intershell correlation than were needed for the  $K$  shell. The predictions of Gilbert,<sup>19</sup> that the "Coulomb hole" has a complicated structure when described by  $r_{ij}$  coordinates for a pair of electrons  $i, j$  having an angular dependence (thus resulting in only slowly convergent Hylleraas-type expansions for electrons of this spatial type), are tentatively confirmed by these calculations.

It is important to compare this calculation with two very refined CI calculations that have been performed. Using a one-electron basis of approximate pair natural spin orbitals Bunge and Peixoto<sup>13</sup> obtained an energy of  $-128.8868$  hartree ( $\sim 88\%$  of the correlation energy) from a CI expansion containing 231 terms formed from a determinantal space of dimension 5343. Recently Sasaki and Yoshimine<sup>20</sup> carried out an exhaustive CI calculation and obtained an energy of  $-128.9168$  hartree ( $\sim 96\%$  of the correlation energy). Our results and discussion suggest that in order to obtain energies which are comparable with these CI values further investigations on the CI-Hy method are required, with particular reference to producing improved computer programs and methods to efficiently evaluate the difficult three- and four-electron integrals, so that calculations using a much larger configuration set than the one presented in this work can be performed. Furthermore, such research will be necessary before the important extension of including terms in the configuration set which are antisymmetrized products of Hartree-Fock-type orbitals with  $r_{ij}$  factors can be carried out.

#### ACKNOWLEDGMENT

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- <sup>1</sup>J. S. Sims and S. A. Hagstrom, Phys. Rev. A 4, 908 (1971).
- <sup>2</sup>J. S. Sims, S. A. Hagstrom, D. Munch, and C. F. Bunge, Phys. Rev. A 13, 560 (1976).
- <sup>3</sup>J. S. Sims and R. C. Whitten, Phys. Rev. A 8, 2220 (1973). J. S. Sims and J. R. Rumble, Phys. Rev. A 8, 2231 (1973). J. S. Sims, S. A. Hagstrom, and J. R. Rumble, Phys. Rev. A 13, 242 (1976).
- <sup>4</sup>J. S. Sims and S. A. Hagstrom, J. Chem. Phys. 55, 4699 (1971).
- <sup>5</sup>A. W. Weiss, Phys. Rev. 122, 1826 (1961).
- <sup>6</sup>H. M. James and A. S. Coolidge, Phys. Rev. 49, 688 (1936).
- <sup>7</sup>S. Larrson, Phys. Rev. 169, 49 (1968).
- <sup>8</sup>In rederiving the formulas presented in Ref. 4 we noted that there is a printing error on p. 4703. The 17th  $X$  function in  $J_5$  should include  $N_1 + 1 + N_{12} + s$ , not  $N_1 + 1 - N_{12} + s$ .
- <sup>9</sup>E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge U.P., Cambridge, England, 1963).
- <sup>10</sup>C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Rev. Mod. Phys. 32, 186 (1960).
- <sup>11</sup>J. S. Sims and S. A. Hagstrom, Int. J. Quantum Chem. 9, 149 (1975).
- <sup>12</sup>J. W. Viers, F. E. Harris, and H. F. Schaefer, Phys. Rev. A 1, 24 (1970).
- <sup>13</sup>C. F. Bunge and E. M. A. Peixoto, Phys. Rev. A 1, 1277 (1970).
- <sup>14</sup>C. F. Bunge, Phys. Rev. 168, 92 (1968).
- <sup>15</sup>T. L. Barr and E. R. Davidson, Phys. Rev. A 1, 644 (1970).
- <sup>16</sup>J. F. Perkins, Phys. Rev. A 8, 700 (1973).
- <sup>17</sup>One such extension that would lead to a large saving in computer time would be the initial storage of all the  $X$ -type auxiliary integrals, defined in Eq. (15), which are repeated many times in the integral formulas (Ref. 4). About  $6.0 \times 10^6$  bytes would be required to do this, but the use of virtual memory facilities or the development of efficient methods for manipulation of these auxiliary integrals on magnetic tape might well make such an approach possible.
- <sup>18</sup>H. F. Schaefer, *The Electronic Structure of Atoms and Molecules* (Addison-Wesley, Reading, Mass., 1972).
- <sup>19</sup>T. C. Gilbert, Rev. Mod. Phys. 35, 491 (1963).
- <sup>20</sup>F. Sasaki and M. Yoshimine, Phys. Rev. A 9, 17 (1974).
- <sup>21</sup>The arguments given in Ref. 1. suggest that  $\chi_1$  is a suitable spin function for this calculation. However, it is possible that introduction of other spin functions could have some importance. This is under investigation.